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## IRON AND STEEL INSTITUTE

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K. HEADLAM-MORLEY

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## PREFACE.

THE present volume contains one report and sixteen papers presented at the Autumn Meeting held in Sheffield on December 10th, 1942; of these, the report and ten papers were presented under the auspices of the Joint Research Committees of the Institute and the British Iron and Steel Federation. The discussions and correspondence to which these give rise are also included, together with the authors' replies. In addition, discussion on a Sub-Committee Report and on a paper included in the No. I. volume for the year will be found in the present book, together with the respective replies.

The foregoing papers, together with the Minutes of Proceedings of the Meeting and biographical notes on deceased Members are included in Section I. of this *Journal*. Section II. is devoted to a survey of the literature on the manufacture and properties of iron and steel, and kindred subjects, and consists of a collection of abstracts of articles from the Transactions and Proceedings of scientific societies and from the technical press. This Section also contains reviews of recent books and bibliographies of literature dealing with the manufacture and properties of iron and steel. The matter included in this Section has already appeared in the *Bulletin of The Iron and Steel Institute*, which is issued monthly.

In front of the title-page are inserted lists of Bibliographies, Special Reports and Translations issued by the Institute.

4, GROSVENOR GARDENS,

LONDON, S.W. 1.

March 31st, 1943 .



# CONTENTS.

LIST OF BIBLIOGRAPHIES . . . . .	PAGE i
LIST OF SPECIAL REPORTS . . . . .	i
LIST OF TRANSLATIONS . . . . .	iii
LIST OF COUNCIL AND OFFICERS . . . . .	vi
PREFACE . . . . .	vii
LIST OF PLATES . . . . .	xi
ABBREVIATIONS USED IN THE TEXT . . . . .	xii

## SECTION I.—Minutes of Proceedings and Papers.

### AUTUMN MEETING, 1942.

Autumn Meeting in Sheffield . . . . .	1P
Obituary . . . . .	1P
Changes on the Council . . . . .	2P
Andrew Carnegie Research Grants . . . . .	2P
Ballot for Election of New Members and Associates . . . . .	2P
Complete List of Papers Presented at the Autumn Meeting in Sheffield, 1942 . . . . .	5P
Vote of Thanks to the President . . . . .	7P
“The Linings of Large Basic Open-Hearth/Tilting Furnaces.” By A. Jackson . . . . .	9P
“Investigations on ‘Falling’ Blast-Furnace Slags.” By T. W. Parker, M.Sc., Ph.D., A.I.C., and J. F. Ryder, B.Sc. . . . .	21P
“The Production in Rotary Furnaces of Steel for Castings.” By F. A. Lemon, M.I.Mech.E., and Hugh O’Neill, M.Met., D.Sc., with Appendices by T. Fletcher and J. N. Bradley, A.R.S.M., B.Sc. . . . .	53P
“A Study of some Soluble Inhibitors, with Special Reference to Heat Transfer and Water-Line Attack.” By R. S. Thornhill, Ph.D., and U. R. Evans, Sc.D. (Paper No. 7/1942 of the Corrosion Committee) . . . . .	73P
“Tests on the Corrosion of Buried Ferrous Metals.” By J. C. Hudson, D.Sc., A.R.C.S., T. A. Banfield, Ph.D., A.R.C.S., and H. A. Holden, B.Sc., A.R.C.S. (Paper No. 6/1942 of the Corrosion Com- mittee (submitted by the Sub-Committee on the Corrosion of Buried Metals)) . . . . .	107P
“The First Cast-Iron Cannon made in England.” By H. Schubert, M.A., D.Phil. . . . .	131P
“The Influence of Tin on Alloy Steels.” By G. R. Bolsover and S. Barraclough . . . . .	141P
“The Crystal Structures of Fe, FeO and Fe <sub>3</sub> O <sub>4</sub> and their Interrelations.” By H. J. Goldschmidt, M.Sc. . . . .	157P
“The Determination of the Solubility of Hydrogen in Iron and Iron Alloys.” By Professor J. H. Andrew, D.Sc., H. Lee, B.Eng., Ph.D., and A. G. Quarrell, B.Sc., Ph.D. (Paper No. 4/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee)) . . . . .	181P



"The Formation of Hair-Line Cracks.—Part I." By Professor J. H. Andrew, D.Sc., A. K. Bose, B.Met., G. A. Geach, M.Sc., Ph.D., and H. Lee, B.Eng., Ph.D. (Paper No. 5/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee)) . . . . .	193P
"The Formation of Hair-Line Cracks.—Part II." By Professor J. H. Andrew, D.Sc., A. K. Bose, B.Met., Ph.D., H. Lee, B.Eng., Ph.D., and A. G. Quarrell, Ph.D., F.Inst.P. (Paper No. 6/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee)) . . . . .	203P
"An Ingot of Rimmed Steel made by the Basic Open-Hearth Process." By D. Binnie, Ph.D. (Paper No. 13/1942 of the Committee on the Heterogeneity of Steel Ingots) . . . . .	283P
"Rimming Steel. Comparative Study of Three Ingots Received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France." By J. Mitchell. (Paper No. 12/1942 of the Committee on the Heterogeneity of Steel Ingots) . . . . .	295P
"Rimming Steel. Report on Four Ingots of Basic Bessemer Steel." By J. Mitchell. (Paper No. 14/1942 of the Committee on the Heterogeneity of Steel Ingots) . . . . .	327P
"Rimming Steel.—Additional Studies of the Composition Variation from Outside to Centre." By T. Swinden, D.Met. (Paper No. 15/1942 of the Committee on the Heterogeneity of Steel Ingots) . . . . .	345P
"A Note on Diffusion in Rimming Steel on Soaking at about 1300° C." By T. Swinden, D.Met., and W. W. Stevenson, A.I.C. (Paper No. 16/1942 of the Committee on the Heterogeneity of Steel Ingots) . . . . .	357P
"Second Report of the Moulding Materials Sub-Committee of the Steel Castings Research Committee." (Paper No. 3/1942 of the Steel Castings Research Committee (submitted by the Moulding Materials Sub-Committee)) . . . . .	393P
Further discussion on "First Report of the Standard Methods of Analysis Sub-Committee of the Committee on the Heterogeneity of Steel Ingots" . . . . .	467P
Further discussion on the paper entitled "On the Carbide and Nitride Particles in Titanium Steels." By William Hume-Rothery, M.A. (Oxon), D.Sc. (Oxon), F.R.S., Geoffrey Vincent Raynor, M.A. (Oxon), Ph.D. (Oxon), and Alexander Torrance Little, B.Sc. (Glasgow) . . . . .	481P
Obituary . . . . .	489P
SECTION II.—A Survey of Literature on the Manufacture and Properties of Iron and Steel, and Kindred Subjects . . . . .	1A
INDEX . . . . .	1

## LIST OF PLATES.

Plates I. and II.	Illustrating Parker and Ryder's paper	<i>Between pp.</i>	48P	<i>and</i>	49P
III. and IV.	Illustrating Lemon and O'Neill's paper	„	56P	„	57P
V.	Illustrating Thornhill and Evans' paper . . . .				<i>To face p.</i> 94P
VI. to VIII.	Illustrating Andrew, Bose, Geach and Lee's paper . . .	<i>Between pp.</i>	200P	<i>and</i>	201P
IX. to XVI.	Illustrating Andrew, Bose, Lee and Quarrell's paper .	„	232P	„	233P
XVIA. and XVIb.	Illustrating discussion on Hydrogen Solubility and Hair-Line Cracks .	„	262P	„	263P
XVII. to XXIV.	Illustrating Binnie's paper . . . .	„	288P	„	289P
XXV. to XXVII.	Illustrating Mitchell's (Denain Ingots) paper . . . .	„	296P	„	297P
XXVIII. and XXIX.	Illustrating Mitchell's (Basic Bessemer Ingots) paper .	„	336P	„	337P
XXX. to XXXIII.	Illustrating Swinden's paper . . . .	„	352P	„	353P
XXXIV. to XXXVII.	Illustrating Swinden and Stevenson's paper . . . .	„	360P	„	361P
XXXVIIA.	Illustrating discussion on Rimming Steel . . . .				<i>To face p.</i> 376P
XXXVIII. and XXXIX.	Illustrating Second Report of the Moulding Materials Sub-Committee .	<i>Between pp.</i>	412P	<i>and</i>	413P

## ABBREVIATIONS USED IN TEXT.

A.	Ångström unit(s).	kg.	kilogramme(s).
A.C.	air-cooled; alternating current.	kg.cal.	kilogramme-calory; -calories.
A.H.	air-hardened.	kg.m.	kilogramme-metre(s).
amp.	ampère(s).	km.	kilometre(s).
amp.hr.	ampère-hour(s).	kVA.	kilovolt-ampère(s).
atm.	atmosphere(s) (pressure).	kW.	kilowatt(s).
Bé.	Baumé (scale).	kWh.	kilowatt-hour(s).
b.h.p.	brake horse-power.	lb.	pound(s).
B.o.T.	Board of Trade.	L.F.	low-frequency.
B.Th.U.	British thermal unit(s).	m.	metre(s).
C.	centigrade (scale).	m.amp.	milliampère(s).
cal.	calory; calories.	mV.	millivolt(s).
c.c.	cubic centimetre(s).	max.	maximum.
c.d.	current density.	mg.	milligramme(s).
c.g.s.	centimetre-gramme-second unit(s).	min.	minimum; minute(s).
cm.	centimetre(s).	ml.	millilitre(s).
coeff.	coefficient.	mm.	millimetre(s).
const.	constant(s).	m.m.f.	magnetomotive force.
c.p.	candle-power.	N.	normal (solution).
cu.	cubic.	N.T.P.	normal temperature and pressure.
cwt.	hundredweight(s).	O.H.	open-hearth; oil-hardened.
D.C.	direct current.	O.Q.	oil-quenched.
dia.	diameter(s).	oz.	ounce(s).
dm.	decimetre(s).	p.d.	potential difference.
e.m.f.	electromotive force.	pH	hydrogen-ion concentration.
F.	Fahrenheit (scale).	r.p.m.	revolutions per minute.
ft.	foot; feet.	sec.	second(s).
ft.lb.	foot-pound(s).	sp. gr.	specific gravity.
g.	gramme(s).	sq.	square.
gal.	gallon(s).	T.	tempered.
H.F.	high-frequency.	temp.	temperature.
h.p.	horse-power.	V.	volt(s).
h.p.hr.	horse-power-hour(s).	VA.	volt-ampère(s).
hr.	hour(s).	Wh.	watt-hour(s).
in.	inch; inches.	W.Q.	water-quenched.
in.lb.	inch-pound(s).	yd.	yard(s).
K.	absolute temperature (Kelvin scale).	°	degree(s).



SECTION I.

*MINUTES OF PROCEEDINGS  
AND PAPERS OF  
THE IRON AND STEEL INSTITUTE.*

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AUTUMN MEETING

1942

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# MINUTES OF PROCEEDINGS

AND

## PAPERS AND DISCUSSIONS

AT THE

### AUTUMN MEETING IN SHEFFIELD, 1942.

THE AUTUMN MEETING OF THE IRON AND STEEL INSTITUTE was held at the Royal Victoria Station Hotel, Sheffield, on Thursday, 10th December, 1942, at 2.30 P.M.; the PRESIDENT (Mr. James Henderson) was in the Chair. There was an interval for tea from 4.30 to 5.15 P.M., and the proceedings closed at 6.30 P.M. By arrangement, the Meeting was a Joint Meeting with the Sheffield Society of Engineers and Metallurgists, the Sheffield Metallurgical Association and the Sheffield Branches of the Institute of British Foundrymen and the Refractories Association of Great Britain.

The PRESIDENT (Mr. James Henderson), in opening the Meeting, welcomed the Members and expressed their pleasure that it was possible again to hold an Institute Meeting in this hospitable and famous centre of steelmaking, Sheffield, and that local Societies were once again collaborating.

The Minutes of the previous Meeting were taken as read and signed.

#### OBITUARY.

The PRESIDENT: We have to mourn the death of Monsieur Eugène Schneider, which took place on 17th November, 1942; he became a Member of the Institute in 1890 and was our President in 1918-1920. Members will also have been grieved to hear of the death of Mr. G. C. Lloyd, which occurred on 10th July, 1942; he was Assistant Secretary to the Institute from 1900-1904 and Secretary from 1909-1933. He was a very dear friend of many of us and we regret his passing. I will ask you to stand for a moment in silence.

The Members stood for a few moments in silent tribute.



## CHANGES ON THE COUNCIL.

The SECRETARY (Mr. K. Headlam-Morley) announced that, in accordance with Bye-Law 10, the following Vice-Presidents and Members of Council would retire in rotation at the Annual General Meeting in 1943 :

*Vice-Presidents* : Mr. Arthur Dorman, Mr. J. S. Hollings and Mr. Fred Clements.

*Members of Council* : Professor J. H. Andrew, Mr. P. B. Brown, Mr. J. R. Menzies-Wilson, Capt. H. Leighton Davies, C.B.E., and Mr. I. F. L. Elliot.

## ANDREW CARNEGIE RESEARCH GRANTS FOR 1942.

The SECRETARY announced that the following Andrew Carnegie Research Grants had been awarded by the Council :

H. J. MERCHANT (Messrs. S. D. F. (Kidderminster), Ltd., Kidderminster)—£100 in aid of an investigation of the attributes of electrolytic polishing for ferrous metallography.

B. H. MASON (Stockholm University, Sweden)—£50 in aid of an investigation of the  $\text{FeO-Fe}_2\text{O}_3\text{-MnO-Mn}_2\text{O}_3$  system.

## BALLOT FOR ELECTION OF NEW MEMBERS AND ASSOCIATES.

Dr. D. BINNIE (Irlam, near Manchester) and Mr. G. R. LEWINGTON (London) were appointed scrutineers of the ballot for the election of new Members and Associates, and they reported that the following seventy Members and forty-six Associates had been elected :

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McLEAN, HECTOR MURRAY, A.I.C. . . . .	Witton, Birmingham.
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TEDDS, DENNIS FREDERICK BERNARD . . . . .		Bristol.
THOMAS, LESLIE ALBERT . . . . .		Prestwich, Lancs.
TINSLEY, DEREK . . . . .		Croydon, Surrey.
TOOTLE, CHARLES RONALD . . . . .		Rugby.
WALKER, ALEXANDER WILLIAMSON . . . . .		Rugby.
WILLIAMS, ALBERT ETHERIDGE . . . . .		Cardiff.
WILLIAMS, LAURANCE HENRY . . . . .		London.
WILLIAMS, SAMUEL ROY . . . . .		London.
WILLIS, KENNETH . . . . .		Middlesbrough.

*Complete List of Papers Presented at the Autumn Meeting  
in Sheffield, 1942.*

- J. H. ANDREW, A. K. BOSE, G. A. GEACH and H. LEE : "The Formation of Hair-Line Cracks.—Part I." (Paper No. 5/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).)
- J. H. ANDREW, A. K. BOSE, H. LEE and A. G. QUARRELL : "The Formation of Hair-Line Cracks.—Part II." (Paper No. 6/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).)
- J. H. ANDREW, H. LEE and A. G. QUARRELL : "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys." (Paper No. 4/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).)
- D. BINNIE : "An Ingot of Rimmed Steel made by the Basic Open-Hearth Process." (Paper No. 13/1942 of the Committee on the Heterogeneity of Steel Ingots.)
- G. R. BOLSOVER and S. BARRACLOUGH : "The Influence of Tin on Alloy Steels."
- H. J. GOLDSCHMIDT : "The Crystal Structures of Fe, FeO and Fe<sub>3</sub>O<sub>4</sub> and their Interrelations."
- J. C. HUDSON, T. A. BANFIELD and H. A. HOLDEN : "Tests on the Corrosion of Buried Ferrous Metals." (Paper No. 6/1942 of the Corrosion Committee (submitted by the Sub-Committee on the Corrosion of Buried Metals).)
- A. JACKSON : "The Linings of Large Basic Open-Hearth Tilting Furnaces."
- F. A. LEMON and HUGH O'NEILL : "The Production in Rotary Furnaces of Steel for Castings." With Appendices by T. FLETCHER and J. N. BRADLEY.
- J. MITCHELL : "Rimming Steel.—Comparative Study of Three Ingots received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France." (Paper No. 12/1942 of the Committee on the Heterogeneity of Steel Ingots.)
- J. MITCHELL : "Rimming Steel.—Report on Four Ingots of Basic Bessemer Steel." (Paper No. 14/1942 of the Committee on the Heterogeneity of Steel Ingots.)

(Continued.)

*(Complete List of Papers Presented at the Autumn Meeting  
in Sheffield, 1942 (continued).)*

T. W. PARKER and J. F. RYDER: "Investigations on 'Falling' Blast-Furnace Slags."

H. SCHUBERT: "The First Cast-Iron Cannon made in England."

T. SWINDEN: "Rimming Steel.—Additional Studies of the Composition Variation from Outside to Centre." (Paper No. 15/1942 of the Committee on the Heterogeneity of Steel Ingots.)

T. SWINDEN and W. W. STEVENSON: "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C." (Paper No. 16/1942 of the Committee on the Heterogeneity of Steel Ingots.)

R. S. THORNHILL and U. R. EVANS: "A Study of some Soluble Inhibitors with Special Reference to Heat Transfer and Water-Line Attack." (Paper No. 7/1942 of the Corrosion Committee.)

"Second Report of the Moulding Materials Sub-Committee of the Steel Castings Research Committee." (Paper No. 3/1942 of the Steel Castings Research Committee (submitted by the Moulding Materials Sub-Committee).)

SECTION I. Introduction and Summary.

SECTION II. Moulding Sands.

Part 1. Examination of Moulding Sands.

Part 2. The Effect of Milling on the Properties of Moulding Sand.

Part 3. The Effect of Surface-Tension-Reducing Agents on the Strengths of Moulding Sands.

Part 4. The Permeability of Moulding Sands.

Part 5. Thermal Expansion of Sand Mixtures Containing Clays.

Part 6. The Use of "Insulating" Sands.

Part 7. Conclusion and Recommendations.

SECTION III. Clays.

Part 1. The Use of Fullers' Earth in Steel Foundries.

Part 2. Report on Clays other than Fullers' Earth.

SECTION IV. Core Compounds and Core-Sand Mixtures.

PRESENTATION OF PAPERS.

A List of all the papers included in the programme of the Meeting will be found above; the following were presented for verbal discussion:

*Afternoon Session.*

A discussion on rimming steel based on the following five papers:

"An Ingot of Rimmed Steel made by the Basic Open-Hearth Process," by D. BINNIE.

"Rimming Steel.—Comparative Study of Three Ingots Received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France," by J. MITCHELL.

"Rimming Steel.—Report on Four Ingots of Basic Bessemer Steel," by J. MITCHELL.

"Rimming Steel.—Additional Studies of the Composition Variation from Outside to Centre," by T. SWINDEN.

“ A Note on Diffusion in Rimming Steel on Soaking at about 1300° C., ”  
by T. SWINDEN and W. W. STEVENSON.

*Evening Session.*

“ Second Report of the Moulding Materials Sub-Committee of the Steel Casting Research Committee.”

At the conclusion of the Meeting the President, on behalf of the Council, thanked the authors for their papers.

VOTE OF THANKS TO THE PRESIDENT.

Dr. W. H. HATFIELD, F.R.S. (Vice-President), moved a vote of thanks to Mr. Henderson for presiding over the Meeting. The President replied briefly.

The proceedings then terminated.



# THE LININGS OF LARGE BASIC OPEN-HEARTH TILTING FURNACES.<sup>1</sup>

BY A. JACKSON (APPLEBY-FRODINGHAM STEEL CO., LTD., SCUNTHORPE).

## SYNOPSIS.

The author first deals with the problem of the linings of large basic open-hearth tilting furnaces from the viewpoint of lining stability when the furnace is tilted, particularly with regard to the lining on the charging side. Then two types of operation and the resultant methods of fettling are briefly outlined. The causes of excessive hearth wear are enumerated, and the resultant effects on the brickwork of the hearth and linings described. Further, the materials now being used for the brickwork of the furnace body and for lining maintenance are discussed. Future prospects are briefly reviewed, and a brief summary of the brick consumptions on two modern furnaces, from which over half a million tons of ingots had been cast, is given in an Appendix.

### *Operating Conditions in Tilting Furnaces.*

LARGE basic open-hearth tilting furnaces are designed primarily to work with large percentages of relatively impure molten iron.

For economic reasons these furnaces are of large capacity, usually charging a minimum of 200 tons. On account of the high structural cost they utilise a deep bath, generally in excess of 33 in., with steep sides, which when working will probably be at an angle exceeding 60° to the horizontal. This angle is far greater than the normal angle of rest of the dolomite fettling as applied during working.

For tapping and slagging the furnaces will tilt some 35° and 15° respectively, giving a total movement of about 50° as a maximum (see Fig. 1).

From the viewpoint of front-lining stability the tapping angle (35° maximum towards the pit) is important, and this angle can be minimised by the use of a tap-hole situated as near as possible to the furnace bottom. The fact that this necessitates a greater tilt in the opposite direction when closing the tap-hole has normally no appreciable effect on the stability of the back lining.

In the Appleby tilting furnaces the steel casing of both the front and back of the furnace is at about 80° to the horizontal. The back lining, which is of uniform thickness from sill level to roof, will only just pass the vertical even when the furnace tilts its maximum angle towards the charging side; thus, unless serious undermining has taken place, there is no danger of this brickwork becoming so unstable as to fall into the bath should the furnace ever be tilted to its maximum of 15°.

<sup>1</sup> Received June 15, 1942.



The problem of the front lining at tapping is far more difficult. In the first place this lining is tapered down from sill level to roof,

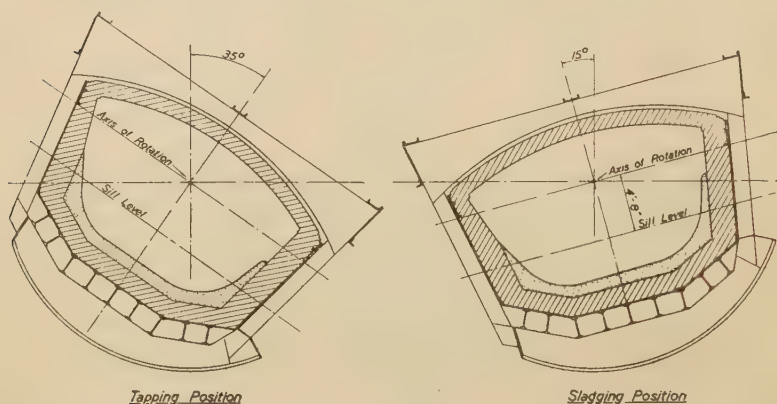


FIG. 1.—Outline Section of Q Furnace.

thus reducing its angle from about  $80^\circ$  on the outer steel plate to about  $72^\circ$  inside the lining. A new lining, without undermining or slag-level wear, therefore, passes the vertical when the furnace is tilted only half of its normal travel towards the tapping side, and this angle of, say,  $18^\circ$  is exceeded at practically every tap and, of course, at the time when the furnace is at maximum temperature and the under-cutting action of the slag at bath level is a maximum for that particular charge.

The normal instability of the front lining is thus demonstrated. Its tendency to fall is minimised by the use of relatively light silica bricks in the upper part, bonded into the roof. In this case the face of the bricks will be so fused after a few charges that the roof and lining will form an almost monolithic structure. This can be contrasted with a chrome-magnesite lining, which is much heavier, does not frit and bond nearly so well and may even be subjected to "growth" near the roof and under-cutting at sill level, thus materially increasing the tendency to become top-heavy. These factors are borne out in practice by the tendency of chrome-magnesite linings to fall out and collapse at tapping.

The first essential for lining stability is that the foundation should be solid and of adequate thickness at sill level. This must be attained by the use of hard-wearing brickwork and good fettling throughout the furnace campaign. The necessity for good-quality dolomite for fettling is fundamental to the reduction of the quantity of magnesite used per ton of steel produced.

*Fettling of Tilting Furnaces.*

Tilting furnaces may be operated in two ways :

- (a) Empty after each charge.
- (b) Leave all the refining slag and some steel in the furnace at tapping.

The former method usually uses higher percentages of scrap than the latter to obtain optimum results.

Fettling of furnaces using the former method will give a bank with an angle about equal to the angle of rest of dolomite. The base of the bank will extend some 4 ft. into the furnace hearth both front and back. This gives a serious reduction in capacity and in consequence reduced output; furthermore a furnace does not work so well with banks of this shape as when they are more nearly vertical. The rate of output is further reduced by emptying the furnace each time. The dolomite consumption is fairly high, as the whole of the hearth is subjected to slag action.

Due to the thick banks the degree of stability of the front lining should be fairly high and the magnesite usage low. The production will not be as high as it could be. Furnaces operating on this method should require very few magnesite bricks in the banks, as the dolomite cover is very thick in most places and stabilised dolomite bricks could be largely used.

In the second method, it is not possible to fettle from the bottom, as the bath will contain 12-20 in. of liquid after tapping. In any case, this is seldom necessary, as the liquid remaining in the furnace at tapping protects the lower portion of the hearth.

To fettle, the slag is thickened by the addition of a portion of the charge and the dolomite rests on the almost solid slag. The bulk of it should burn on during subsequent operations. In this instance fettling is only applied round about the normal slag line, which is, of course, the point at which maximum cutting takes place. The bath capacity is kept up and gives greater output, and this is further increased by leaving metal and slag in the furnace at tapping. The dolomite consumption is reasonably low, but greater attack of the magnesite brickwork is liable to take place, thus reducing the stability of the upper lining and increasing thereby the magnesite and chrome ore used in its maintenance.

In normal times the increased steel production and increased value of the basic slag do far more than compensate for any extra cost of magnesite materials.

In a tilting furnace working on this latter method, the magnesite brickwork will be gradually worn away throughout the furnace life, due to its being periodically exposed to the action of slag and metal when the dolomite has been worn away.

This periodic attack on the magnesite cannot easily be avoided, as it is caused by the following factors :

- (1) Variation in iron quality, which may give excessive cutting by steel or slag (*e.g.*, increase in silicon content).
- (2) Excessive foaming, which cuts the banks above the normal level; this effect is made worse by the increased flame attack just above the surface of the foam.
- (3) Prolonged refining time (special steels or high-sulphur iron).
- (4) Poor fettling, *e.g.*, not fully burnt in before adding molten metal, or bad placing of the dolomite.
- (5) Badly prepared dolomite, *i.e.*, not fully shrunk.
- (6) Various operational delays to the process.

Most of these factors occur in all furnaces, but in a tilting furnace, in which some slag and metal are left at tapping, the fettling is probably thinner than average, owing to the limitations of the method used for fettling.

To summarise briefly, to obtain good output it is practically unavoidable that the brickwork of the hearth is quite often exposed to slag and metal action. If the bricks are not highly resistant, then the lining is undermined deeply, and this cavity cannot possibly be filled tightly with dolomite; thus sinking and finally collapse will take place. The only satisfactory way to fill deep undercutting is by using a wet chrome-magnesite paste, "placed" with long-handled shovels, and finally covered with dry dolomite.

The collapse of an undermined lining is not generally very sudden, but takes place by the bottom courses sinking at the inner ends, giving ever-widening joints above, and finally a vertical layer will gradually but completely break away. This is followed by another layer after further undermining, and so on. The lining again can only be saved by pasting the ever-widening joints with a wet ground mix.

#### *Types of Bricks for Lining Basis.*

The type of brick necessary to form a basis for the lining must, when in contact with slag or metal, have a high resistance to reaction. It must also have a low shrinkage at high temperatures. These conditions were probably best fulfilled by Austrian magnesites and to a somewhat less extent by bricks produced from the purer magnesites. The latter magnesites could probably be as good as Austrian, but in practice this is often not the case, possibly owing to the greater difficulties involved in the production of bricks from the purer material.

The alternative basic bricks, chrome-magnesite and stabilised dolomite, are definitely less good and wear away relatively rapidly near the sill level. The mode of failure probably differs, in that dolomite bricks are mainly removed by slag attack, whilst chrome-magnesites are susceptible to the attack of molten mixer metal, which, of course, will be present in the early stages of the operation.

The present position regarding the suitability of various basic bricks below sill level is considered at Appleby-Frodingham to be as follows :

*Magnesite*.—These bricks appear (from observations in use) to be slightly less resistant to attack than pre-war types. No equally good substitute for all-round use has been produced.

*Chrome-Magnesite*.—For furnaces using high percentages of molten iron these bricks do show some advantage over dolomite bricks where exposure to metal and slag is to be expected, though they are definitely less good than magnesite. For linings above slag level, the best types are better than straight magnesite.

*Stabilised Dolomite*.—Assuming that no possibility of powdering is involved, these bricks are satisfactory in all positions where they can be well covered with dolomite fettling.

If they become exposed they offer a good resistance to wear by molten steel and are therefore quite good for the furnace bottom if out of contact with slag.

In contact with slag, they wear rapidly, when compared with the magnesite and chrome-magnesite bricks; similarly they cannot be exposed to flame action above slag level, owing to their high spalling tendency and shrinkage.

#### *Linings up to Sill Level.*

*Bottom*.—Our experiments indicate that a  $7\frac{1}{2}$ -in. thickness of magnesite (used as three  $2\frac{1}{2}$ -in. courses) is satisfactory for the furnace bottom. If the frequency with which complete bottoms are renewed and the loss involved in a break-out are considered, there is really no valid reason for reducing this thickness further at the moment. The remainder of the bottom and some 12 in. of the banks can also be put in with dolomite bricks quite safely.

*Front Bank*.—Trials on some fifteen furnaces indicate that dolomite bricks are unsuccessful. They invariably wear rapidly, and so cause undue maintenance on the lining by undermining. Three main factors contribute to this :

(a) More difficulty in inspection and fettling.

(b) A small degree of undermining is very liable to cause failure in the front lining, owing to the considerable angle of tilt at tapping.

(c) In charging, the machine will dump portions of certain materials on the banks and the metal is poured in on this side.

The only satisfactory brick for the front bank at present is magnesite.

*Back Bank*.—The base previously mentioned consists of some 12 in. of dolomite brick, then about 12 in. of magnesite are put on,



followed by not more than 24 in. of dolomite brick. This brings the lining near slag level. Continuation above this point results in back-lining trouble caused by under-cutting and shrinkage of the dolomite bricks. In the several instances where trials were made using more of these bricks, the back lining gradually bowed out from the casing and eventually collapsed. Subsequent examination showed that the bowing outwards commenced in the dolomite portion of the furnace bank; thus the wash-line of the furnace at the back should also be of magnesite. Very careful fettling is essential to give moderate success with stabilised dolomite bricks.

*End Banks.*—About 12 in. of magnesite are used on the bottom, and then dolomite bricks are taken up to sill level. This is successful, because the end banks have little lining weight to support; also the slope is much less steep than at the front and back banks and approximates more nearly to the angle of rest of the dolomite fettling. Good fettling is easy, and the maintenance of a good dolomite coating has no great effect on the furnace capacity. Even here, however, some shrinkage occurs, and the splays are liable to show sinking, with consequent widening of the brick joints. These must be fettled lightly with magnesite paste in the early part of the campaign.

#### *Linings above Sill Level.*

*Splays.*—The dolomite bricks are taken just above sill level and separated by two or three courses of magnesite bricks from the silica above, which is taken right to the roof.

*Back Lining.*—From about sill level chrome-magnesite bricks are used to the roof, with two courses of silica on top. Present chrome-magnesite bricks often show more bursting than pre-war types, but if the thickness of the base of the lining can be maintained these linings are still quite successful.

*Front Lining.*—Magnesite or chrome-magnesite bricks are used to about 12–15 in. above sill level, the remainder to the roof being of silica. Chrome-magnesite pillars have been tried on several occasions, but do not offer any decided aggregate advantage, owing to their liability to fall into the bath.

#### *Maintenance of Linings.*

Linings are patched when necessary with well-ground chrome-magnesite paste. Formerly this paste contained upwards of 70% of magnesite. Experiments have been made using as little as 20% of magnesite, but patching was not so successful; some saving in magnesite was obtained, but greater quantities of paste had to be used. Now a paste containing 40% of magnesite is considered to give reasonable satisfaction, but if equal difficulty were found in obtaining supplies of chrome ore as of magnesite, then a reversion towards a paste of higher magnesite content would result in aggregate savings.



Little paste is used on the back and end linings (splays) of the furnace, the bulk being used to maintain the front.

Some little saving has resulted from commencing the pasting of the linings from a higher level than was previously done, but as undermining is the main problem, the saving is not as great as might have been expected. High-chrome pastes are not as successful as high-magnesite types for slag-line patching; in consequence the use of the 40% magnesite paste for this purpose is conducive to waste.

Trials without pasting have been made, but trouble quickly arose even with chrome-magnesite pillars in place of silica.

### *Future Prospects.*

It is hoped in the near future to perfect a stabilised dolomite cement with which to repair front linings in place of chrome-magnesite. This material will, of course, necessitate a basic lining, and some method will be necessary to tie these bricks to the furnace structure to prevent overbalancing. Water-cooled pipes of various shapes have been experimented with, and have shown some measure of success, but one or two nasty experiences resulting from undetected water leakages preclude this method from the possibility of real success.

Methods using metallic strips welded to the casing are being considered, but as the outer furnace plating forms a continuous structure, the relining would be slowed up, whilst rebuilding of a new lining with the furnace in commission would be impossible if welded strips were found to be essential for structural stability.

Further methods are being considered, but until substantial quantities of this cement have been used it is not possible to forecast how the difficulties will be overcome.

### *Summary.*

(a) Magnesite and chrome-magnesite bricks are not of the same high quality as that attained about three years ago.

(b) Chrome-magnesite bricks are probably still superior to magnesite for the linings of open-hearth tilting furnaces above the slag line.

(c) Stabilised dolomite bricks can be used in part in the lower portions of the hearth to replace magnesite. They must be kept covered with fettling, or their life is poor.

(d) Magnesite bricks are still the only satisfactory bricks for use about the slag line.

(e) Stabilised dolomite cements may replace a reasonable portion of the chrome-magnesite cement used for lining maintenance, if present experiments in manufacture are successful.

(f) The dolomite used for ordinary fettling must be fully shrunk and in good mechanical condition (suitable grading, &c.) to give

the maximum reduction in consumption of magnesite and chrome materials.

APPENDIX.—*Brick Consumption of Two Recently Built 300-Ton Furnaces.*

Working weeks <sup>1</sup>	.	.	.	.	178.6	119
Time working, %	.	.	.	.	90.8	93.3
Total production, Tons	.	.	.	.	347,323	230,863
Tons per working week	.	.	.	.	1,945	1,948
Brick consumption :						
Silica bricks, Lb. per ton	.	.	.	.	16.31	16.74
Firebrick, Lb. per ton	.	.	.	.	1.54	1.16
Magnesite, Lb. per ton	.	.	.	.	1.92	1.22
Chrome-magnesite, Lb. per ton	.	.	.	.	1.13	1.55
Stable dolomite brick, Lb. per ton	.	.	.	.	0.82	0.50
Total brick consumption, Lb. per ton	.	.	.	.	21.72	21.17

<sup>1</sup> The working weeks commence when the furnace is gassed and include all minor repairs.

The author wishes to thank the Management of the Appleby-Frodingham Steel Co., Ltd., for their permission to publish this paper.

### CORRESPONDENCE.

Mr. J. F. WILSON (Horam, Sussex) wrote : In addition to the various values of resistance provided by the different refractories discussed, and, referring in particular to the slag-line, where it is assumed that the bulk of the attack takes place or originates, I would suggest that the author concentrates more on the length and quality of that attack rather than on the resistance value of the various refractories which must eventually overcome it.

On the fourth page the author wrote : " To summarise briefly, to obtain good output it is practically unavoidable that the brick-work of the hearth be quite often exposed to slag and metal action." In suggesting that further consideration of this statement might well be repaid, I would say that on one occasion only have I found such a statement admissible, and on that occasion the fault lay within the process itself.

In that instance the Hoesch process was in operation and the heavy slag-line attack was successfully taken chiefly by the magnesite brick lining, but it was rather punishing work generally. To have attempted such work with the much steeper furnace banks as quoted by the author would certainly have proved more difficult and, probably, more hazardous.

The tilting furnace, however, provides facilities for great opera-

tional resiliency, and, in my opinion, slag-line attack can be sufficiently controlled so as to prevent frequent exposure of the brickwork lining.

Slag-line attack must, in the first instance, be taken as coming from the slag itself, yet, on referring to the six governing factors as quoted by the author on the fourth page, none of these can be said to have any direct reference to this. Factor (1) will, in effect, vary the amount of slag produced, and, while a steady quality of iron is highly desirable, the tilting furnace provides facilities for dealing with such variations. To quote extreme cases: First, where for a period a short basic iron supply was supplemented by 2.5–3% silicon metal, and, secondly, the general week-end practice of assisting a low-capacity metal mixer by using a proportion of direct metal in the steel furnaces, careful slag removal at an appropriate time enabled a high standard of output to be maintained without any noticeable increase in slag-line attack. As the bulk of steel made contained from 0.4% to 0.7% of carbon as tapped from the furnace, it could be said that the banks were well tested.

Regarding factor (2), excessive foaming in a furnace of normal heating capacity can, in my opinion, be checked. Foaming can easily be obtained even with the steel bath at tapping temperature, provided that the carbon content of the steel is sufficiently high, say, over 0.70%, but this can be prevented by the addition of burnt lime. In the earlier and low-temperature stages when this reaction most frequently occurs, the conditions that give rise to it are basically similar, and I would suggest that a low-temperature carbon reaction combined with an inefficient slag blanket is almost sure to foam, and an adjustment of charging procedure which tends to increase the metal-carbon reaction temperature and at the same time provide a more efficient slag blanket should prove beneficial.

For the purposes of constructional discussion it may be advantageous to refer briefly to slag conditions or factors which may give rise to slag-line attack, it being understood that the attack is not meant to include the "boil" on unfritted material or brickwork joints, which usually originates from the metal bath. If we first assume the attack upon the dolomite to be in two distinct stages:

(1) The contamination period, during which the melting point of the dolomite more closely approaches that of the slag, and

(2) the higher-temperature period when the slag will tend to melt the more viscous dolomite,

additional factors may then be considered, such as:

(a) The quantity of slag cover. Besides providing a greater area for attack, the surface superheat is cumulatively higher.

(b) High-temperature-slag/time ratio, *i.e.*, the length of

time during which the finishing or other high-temperature slag is allowed to cover the steel bath.

(c) Slag too highly basic. This can easily occur when the metal charge is in the very low-silicon range, and by injudicious lime addition.

It will be noted that relief obtained from either of the above factors should tend to increase production and reduce furnace wear and tear.

Mr. R. E. H. WILLIAMS (General Refractories, Ltd., Sheffield) wrote: The stability of basic refractory materials and structures is a subject that interests many industries where rotating or tilting furnaces are employed. One feels that, in view of the expenditure at Appleby upon pasting materials, the use of specially shaped chrome-magnesite bricks might be adopted for front-lining construction. It would seem possible to build this lining from sill-level with flat slabs, so that each course, when viewed in plan, showed a flat arch. Bearing in mind the difficulties inherent in the manufacture of special basic bricks, it would appear that shapes approximately 18 in.  $\times$  6 in.  $\times$  3 in. would be the most suitable. If an 18-in. thick lining is sufficient, then the desirable header construction could be adopted.

To retain the end blocks of the arch, a welder would be required for perhaps an hour when the furnace was off for repairs, to fix retaining plates perhaps 6 in. wide between the door-jamb bricks and the flat arches. Longitudinal expansion would be accommodated by the insertion of asbestos sheeting or in other ways. Perhaps steel sheet (or preferably malleable iron) jointing (horizontally) would, despite some of its inherent disadvantages, be most satisfactory in this case, so that the stability of the front-wall pillars would not depend upon the stability of an odd brick here and there, but rather upon the lining as a whole.

The extra cost of "special" as compared with "standard" shapes would be approximately 15% (exclusive of initial mould costs, &c.).

At Appleby it appears that the repairing of deep holes in the bottom and banks has been regarded in the same way as in America. In the latter country extensive use is being made of quick-setting basic compositions having considerable freedom from any tendency to hydrate or shrink at steel-melting temperatures. These compositions can be either straight magnesite or chrome-magnesite. Their chief function is to fill in the bottom of deep holes in the dolomite or magnesite.

In connection with refractory problems generally, one sometimes wonders whether sufficient interchange of views occurs between metallurgical and refractory producers in the United States of America and Great Britain.

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*AUTHOR'S REPLY.*

The AUTHOR wrote : In reply to Mr. Wilson, I did not consider it necessary in this paper to make any reference to the methods used in "reducing the length and quality of the attack," but these factors are of necessity given every consideration in every plant.

With regard to the exposure of the magnesite brickwork to slag attack, the term "quite often" is purely relative, and its significance is given by the quantity of magnesite brick used as indicated in the figures. Some of the usage shown is actually recovered and reground for patching cement.

Slag is not mentioned as a factor influencing slag-line attack, it being understood to be present. The points given are those liable to increase the normal "cutting" effect of slag on the furnace banks.

Factor (1) on p. 12 P normally increases the silica in the slag, as iron variations from cast to cast are seldom known in time to alter the charge for a given furnace. If the silicon is known before charging, then this ceases to become a variable and lime can be added if necessary.

Foaming in a furnace when refining with the carbon in the bath at about 0.70% can undoubtedly be reduced on many occasions by adding burnt lime. This material, however, will not stop foaming in a partially melted hot-metal charge in a furnace burning mixed coke-oven and blast-furnace gas, once that foaming has commenced.

Regarding slag quantity, the tilting furnaces mentioned produce little over 3 cwt. of slag per ton of steel, and often have as little as 1 cwt. per ton on the bath during refining.

The refining time seldom exceeds 2 hr., except in the case of special steels.

Experiments on the lines suggested by Mr. Williams have been considered, but it is doubtful if the suggested skewback plates would support a flat arch for very long, even if they only got to a red heat.

Trials are in hand at the moment in which slotted bricks fixed to the casing are used to repair linings; they are showing some measure of success.



# INVESTIGATIONS ON "FALLING" BLAST-FURNACE SLAGS.\*

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(Figs. 6 to 15 = Plates I. to II.)

## SUMMARY.

An investigation on methods of detecting "falling" blast-furnace slags is described. It is confirmed that the basic cause of falling is the inversion of the high-temperature crystalline form of  $2\text{CaO} \cdot \text{SiO}_2$  to the low-temperature form, with accompanying expansion. Measurement of expansion does not, however, provide an accelerated test for falling. A test, previously proposed by A. Guttmann, making use of the ultraviolet lamp, tends to err on the unsafe side. Two new tests are proposed, both based on using only slag in which no  $2\text{CaO} \cdot \text{SiO}_2$  is present. One of these, suitable for slags which are cooled slowly, *e.g.*, by the "ball" method, depends on the use of an equation, introducing the analytical values for the oxide constituents, and is based on phase equilibrium in the systems, making use of the "suspended equilibrium" hypothesis. The other is a microscope test with polished specimens etched with a reagent which, in blast-furnace slags, is more or less specific for  $2\text{CaO} \cdot \text{SiO}_2$ . These two tests err slightly on the safe side.

## FOREWORD.

BY THE BLAST-FURNACE COMMITTEE OF THE IRON AND STEEL  
INDUSTRIAL RESEARCH COUNCIL.

THE Blast-Furnace Committee of the Iron and Steel Industrial Research Council has had under consideration from time to time the question of blast-furnace slags, with respect to both the reaction inside the furnace and the utilisation of the slag when made.

In the past, a number of British blast-furnace slags have not been marketed, largely because of their liability to disintegrate when air-cooled, which makes them unsuitable for use in tarmacadam or as concrete aggregate. Other slags, while usually quite suitable for these purposes, occasionally had a proportion of material which disintegrated and thereby became unsuitable.

In 1935 the matter was referred to a Panel of the Blast-Furnace Committee. The terms of reference of the Panel were :

- (1) To examine methods of rapid testing of air-cooled slags, particularly with regard to disintegration;
- (2) To examine whether, by suitable methods of foaming, unstable slags could be stabilised.

\* A Report of the Slag Tests Panel to the Blast-Furnace Committee of the Iron and Steel Industrial Research Council, received February 22, 1942.

A report on the second item was made in 1937, in which it was shown that stable products could be made by the foaming process, even from unstable slags.<sup>(1)</sup> The results of the investigation on which this conclusion was based were made available to the British Standards Institution and made possible the production of a British Standard Specification for Foamed Blast-Furnace Slag for Concrete Aggregate, No. 877-1939.

The first item has also been the subject of a detailed investigation at the Building Research Station of the Department of Scientific and Industrial Research, and has included not only the immediate subject of reference but also a comprehensive study of the properties of slag concrete, for it was considered that if air-cooled slag could be shown to be suitable as a concrete aggregate, it would not only increase the sources of aggregate available to the engineer, but would provide, from the producer's point of view, an additional outlet for relatively large quantities of slag. These investigations have now been completed. The conclusions show that concrete of satisfactory quality can be made from blast-furnace slag aggregate, provided that the latter satisfies certain requirements which can be assessed by laboratory tests. This represents a long step forward, since, although slag aggregate has been used in fair quantity abroad, its use in Great Britain has been limited and the material has been regarded with some suspicion. The fact that unsuitable material can be excluded by preliminary tests should go far to remove this suspicion. Indeed, it has proved possible to use the data of the investigation in drafting a British Standard War Emergency Specification for Air-cooled Blast-Furnace Slag Aggregate for Concrete for Structural Purposes, including Roads. This specification is being considered at present by the appropriate Committee of the British Standards Institution, and it is understood that it is likely to be published in the near future.

A report of the investigation of the properties of slag concrete is being prepared for publication. Since the subject-matter is of direct interest to building practice, it is proposed to publish results in a technical journal directly concerned with the building industry. The present report, which has been prepared by Dr. T. W. Parker and Mr. J. F. Ryder, of the Building Research Station, describes the investigation of "falling" slags, especially with reference to laboratory methods of detecting falling. As a result of the work it has been possible to devise two new tests, both of which require certain technical facilities for their operation, but which should not be impossible to carry out as a control measure in works practice. These two tests have also been incorporated in the specification mentioned above.

### 1.—INTRODUCTION.

An essential requirement of any concrete aggregate is that it should be stable. Certain slags are, therefore, at once ruled out as un-



suitable because they disintegrate after solidifying from the molten state. At its worst this results in the originally rock-like mass being converted entirely into a coarse powder. Such slags are termed "falling" slags in the industry. The total quantity of this type that is produced is relatively small compared with the amount of stable slag. Moreover, there is not much danger that falling slags of the type described above would ever be used as an aggregate because the disintegration is complete within a few days of the slag being tapped from the furnace. When the disintegration is less severe, however, it may take place slowly; it may never proceed as far as complete powdering of the mass, so that the appearance becomes only that of a relatively weak, friable solid, or portions only of the main slag mass may fall, the remainder appearing hard and solid. Such material would obviously not be suitable as an aggregate. Though the proportion of slags in this intermediate state is small, it is highly desirable that there should be a test by which falling slags can be distinguished at an early stage after production. The possibility of devising such a test was the main object of the present investigation.

## 2.—PREVIOUS EXPERIENCES.

Experience of falling slags is by no means new to the iron-producing industry, and it has long been known that there is some relation between falling and the chemical composition of a slag. With high contents of CaO in slags the tendency to falling increases, and under the relatively constant conditions of production and cooling of slags at any one works it is almost possible to predict whether or not a slag will fall purely from the determination of its CaO content; a figure of 42% of CaO is one in common use. Other views are that the slag tends to become more prone to falling as the ratio of CaO to  $\text{SiO}_2$  in the slag increases. Knight,<sup>(2)</sup> for example, gives a ratio of 1.3 as being a limiting one above which the slag may be a falling one.

The chemical composition is not the sole factor, however. At least as important is the rate of cooling of the slag from the molten condition. A slag which will fall after the fairly slow cooling conditions of solidification in a 7-ton ladle may be perfectly stable if cooled more rapidly by pouring in thin layers on a slag-bank or into a shallow pit. Even slags which fall completely to a powder after slow cooling may be made perfectly stable by chilling very rapidly with water, as in granulation or foaming processes.

The coincidence of the high lime content with falling has led to the theory that falling is associated with the presence of calcium orthosilicate,  $2\text{CaO}.\text{SiO}_2$ , in the mineral composition of the slag.<sup>(3,4)</sup> This compound is known to exist in three different crystalline forms, the  $\alpha$  form being the stable modification at temperatures over  $1415^\circ\text{C}.$ , the  $\beta$  form between  $1415^\circ\text{C}.$  and  $675^\circ\text{C}.$  and the  $\gamma$  form below  $675^\circ\text{C}.$  The inversion at  $675^\circ\text{C}.$  on cooling is accom-

panied by a change in density which produces a volume increase of about 10%, and it is held that this expansion produces the disintegration of the slag. The influence of rapid cooling in stabilising the slag can be explained on this theory by the assumption that the cooling prevents crystallisation proceeding to equilibrium, part of the slag being chilled to the glassy state. The  $2\text{CaO}.\text{SiO}_2$  either then remains in solution in the glass without having an opportunity to crystallise, or the films of glass round the  $2\text{CaO}.\text{SiO}_2$  crystal grains prevent the inversion from the  $\beta$  to the  $\gamma$  modification. Phenomena similar to the latter are known in the field of Portland cement clinker technology.

The view has also been advanced that falling is caused in some way by the combined sulphur in the slag. Blast-furnace slag acts as a desulphuriser of the iron in the blast-furnace. The higher-limed and the hotter slags are the most efficient desulphurisers, and consequently this type of slag is associated with higher sulphur contents than the lower-lime type.

The methods in use at blast-furnaces to identify falling slag in advance rely to a very large extent on long experience. The appearance of the slag during tapping, its chemical analysis and, sometimes, the appearance of the solidified slag are taken into account. The prediction is only very rarely at fault, but whether or not the evidence used at one works could be applied unchanged to another is very doubtful. A laboratory test utilising examination by ultraviolet light has been proposed by A. Guttman<sup>(4)</sup> (*loc. cit.*, p. 56) and has been used in German specifications for slag aggregate. An examination has been made of it in the present investigation.

### 3.—THE CAUSE OF FALLING.

It is not difficult to show that the calcium orthosilicate theory is the more probable of the two theories outlined in the previous section to account for falling. Synthetic slags containing only  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  as starting products were melted in carbon crucibles in a gas furnace and allowed to cool slowly in the furnace. By regularly increasing the lime content in successive mixes, products were eventually obtained which showed all the characteristic features of a falling slag, whereas when successive additions of  $\text{CaS}$  were made to the starting composition instead of lime a falling product was not obtained, indicating that the sulphur content is not, of itself, concerned in the falling process. It may easily be shown that falling will proceed independently of outside weathering conditions. For example, slags will fall when stored in sealed tins or *in vacuo*; the disintegration is therefore due to a physical or chemical change in the slag itself. When pure  $\beta$   $2\text{CaO}.\text{SiO}_2$  is prepared and allowed to cool, the volume increase in the inversion produces an appearance very similar to that of falling.

The microscope examination of fallen slag powder frequently permits of the identification of  $\beta$  or  $\gamma$   $2\text{CaO}.\text{SiO}_2$  in the powder. A variation of the microscope examination in which a thin section of falling slag was made and examined under the microscope both by the reflected fluorescence from the ultraviolet lamp on the specimen and also by ordinary transmitted light showed that the material which fluoresced yellow was probably  $2\text{CaO}.\text{SiO}_2$ . This was confirmed by preparing a polished surface of a falling slag and scraping out with a needle material which fluoresced yellow under the ultraviolet lamp. This powder was then examined under the microscope by the immersion method and shown to be composed chiefly of  $\beta$  and  $\gamma$   $2\text{CaO}.\text{SiO}_2$ . Portland cement clinker contains  $2\text{CaO}.\text{SiO}_2$ , and as the lime content is reduced, giving an increasing content of this compound, there is an increased tendency for the clinker to "dust" on cooling, after passage through the kiln. The phenomenon of dusting is quite similar to that of falling.

Another indirect confirmation of the hypothesis arises from a laboratory method of stabilising falling slags. If  $2\text{CaO}.\text{SiO}_2$  is heated to the temperature range of  $\beta$  stability, say, at about  $1350$ – $1400^\circ\text{C}$ ., in the presence of a few tenths per cent. of boric oxide, the  $\beta \rightarrow \gamma$  inversion is inhibited on cooling, the  $\beta$   $2\text{CaO}.\text{SiO}_2$  persisting indefinitely at ordinary temperatures. Similarly the addition of a few tenths per cent. of boric oxide in preparing slags in the laboratory will suppress the falling phenomenon.

The combination of this evidence makes it almost certain that  $2\text{CaO}.\text{SiO}_2$  is the cause. However, this simple explanation does not cover all the factors involved. The problem of the stabilisation of the higher-temperature forms of  $2\text{CaO}.\text{SiO}_2$  at ordinary temperatures is not completely solved. A theory has been put forward that the inversion of the  $\beta$  into the  $\gamma$  form takes place rapidly, but that the  $\alpha \rightarrow \beta$  inversion is sluggish, in order to account for the enhanced stability, or slowing of the rate of inversion to the  $\gamma$  form, when the compound is heated above  $1415^\circ\text{C}$ . and quenched rapidly. After cooling under these conditions it is possible to retain the high-temperature form for some time. On the other hand, it is almost impossible to retain the high-temperature form by quenching from below  $1415^\circ\text{C}$ . without also having present a stabiliser such as boric oxide.

Part of the ternary system  $\text{CaO}-\text{SiO}_2-\text{B}_2\text{O}_3$  has been investigated by E. P. Flint and L. S. Wells.<sup>(5)</sup> It is found in this system that solid solutions of  $\text{CaO}.\text{B}_2\text{O}_3$ ,  $2\text{CaO}.\text{B}_2\text{O}_3$  and  $5\text{CaO}.\text{B}_2\text{O}_3.\text{SiO}_2$  in  $2\text{CaO}.\text{SiO}_2$  can take place, and that the  $\alpha \rightarrow \beta$  inversion temperature is lowered with the solid solution. It follows that in the presence of  $\text{B}_2\text{O}_3$  there is a greater tendency to quench from the  $\alpha$  state and hence render the product more stable at ordinary temperature. However, the main stabilising effect seems to be due to the formation of tenacious glassy films round the orthosilicate grains which prevent mechanically the expansion of the crystal which is

necessary for the inversion to take place. Although this is the only available theory of stabilisation, it is difficult to reconcile it with the falling of slags when the mechanical effect of the contraction on cooling might be expected to exert at least as much restraint as a thin film of a boric-oxide-containing glass, but actually has often no such effect.

Another difficulty is the observed time-period of falling of slags. It would be expected that falling would begin as soon as the temperature of the slag had passed the  $\beta \rightarrow \gamma$  inversion point. Frequently, however, the slag is quite cold before falling is observed and, in fact, some days may elapse before falling becomes apparent. On the basis of a certain amount of data described below, an explanation may be that part at least of the  $\beta \rightarrow \gamma$  inversion takes place immediately on passing the  $\beta \rightarrow \gamma$  inversion point, but that falling may not become apparent until other influences, such as weathering or rain, have had an opportunity to act. This is not inconsistent with the point made earlier that falling can take place without outside influences. In the worst cases this observation is correct; in less severe cases weathering may be required to make it obvious that falling has occurred.

#### 4.—TESTS FOR FALLING SLAG.

##### (a) *Volume-Expansion Tests.*

The relatively large expansion occurring in the inversion from  $\beta$  to  $\gamma$   $2\text{CaO} \cdot \text{SiO}_2$  affords one method of following the course of the transformation. Accordingly tests were made on falling slags, using a dilatometer technique described in an earlier publication.<sup>(1)</sup> The first tests were made on spoon samples of slags from hematite iron production. By adjusting the size of the spoon it was possible to secure samples in which the falling was delayed sufficiently to allow for time of transport from the works to the Building Research Station. In the dilatometer tests some of these samples showed a marked expansion; an example of the curve of expansion with time for one of these slags was given in the earlier paper. However, further study of the test showed irregular results; it could not always be shown that a slag which was obviously falling was also suffering a volume expansion. Examples of the data obtained are included in Table I. The slags marked as "Hematite" were all of the type showing falling by the normal cooling methods. Those from *B18* to *B35* inclusive were from one works while *B36* to *B40* were from another. The samples *B19*, *B41*, *B51* and *B52* were all from slags known to be stable and having a good reputation as a roadmaking material.

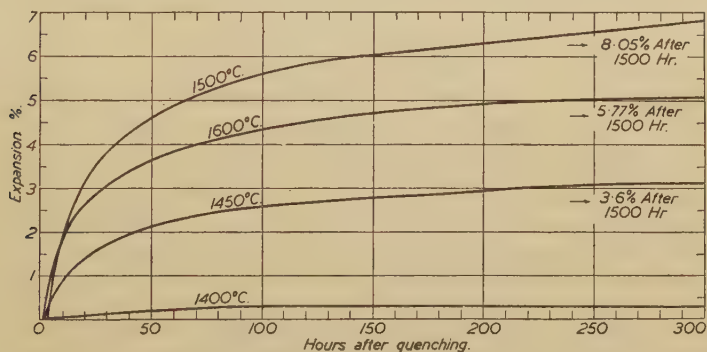
During the course of these tests, an opportunity was taken to make similar measurements on samples of pure  $2\text{CaO} \cdot \text{SiO}_2$  after quenching from various temperatures. Typical examples of curves obtained by plotting expansion against time are shown in Fig. 1.



TABLE I.—Results of Expansion Tests.

Sample No.	Type and Nature of Sample.	Ex- pansion, % (vol.).	Remarks.
B18	Hematite—small spoon	0.42	Expansion ceased at 50 days.
B19 <sup>(3)</sup>	Cleveland—large piece	Nil	Duration of test 200 days.
B22	Hematite—large spoon. Two samples taken at same time	0.25 0.85	Expansion ceased at 50 days. Still expanding at 230 days.
B25	Hematite—large spoon	0.08	Expansion ceased at 15 days.
B28	Hematite—small spoon	0.07	Still expanding at 200 days.
B34	Hematite—large piece, stable for 6 months be- fore test	0.04	Expansion ceased at 80 days.
B35	Hematite—large piece, stable for 2 weeks be- fore test	0.02	" " 80 "
B36	Hematite—spoon sample	0.05	" " 110 "
B38	" " "	0.09	" " 170 "
B40 <sup>(1)</sup>	" " "	0.14	Still expanding at 120 days.
B40 <sup>(2)</sup>	" " "	0.02	Expansion ceased at 50 days.
B41 <sup>(3)</sup>	" " "	Nil	Duration of test 120 days.
B41 <sup>(4)</sup>	" " "	0.01	Still expanding at 120 days.
B51 <sup>(3)</sup>	Basic	Nil	Duration of test 200 days.
B52 <sup>(3)</sup>	Cleveland	0.01	Expansion ceased at 30 days.

- (1) A portion of a spoon sample thought likely to disintegrate.
- (2) A portion of a spoon sample thought likely to be stable.
- (3) Stable slag as used for roads.
- (4) A small sample from the same source as (3) but discarded as crumbly and probably falling.


 FIG. 1.—Dilatometer Tests on  $2\text{CaO}.\text{SiO}_2$ .

The three experiments in which the quenching was carried out above the  $\alpha \rightarrow \beta$  inversion temperature all show expansion, *i.e.*, inversion to the  $\gamma$  form, to be taking place over the 1500-hr. duration of the measurements.



The expansion is most rapid during the early stages of the tests, and for this reason little significance can be attached to the total expansion value measured, because some 2-3 hr. necessarily elapsed before the first measurement was taken in order to permit thermal equilibrium to be established between the dilatometers and the thermostat. The product quenched from  $1400^{\circ}\text{C}$ . (*i.e.*, the  $\beta$  product) shows only a very small expansion during the first 100 hr., because almost complete inversion took place before the product was packed into the dilatometer, *i.e.*, within 30 min. of quenching. This was checked by microscope tests.

The temperature of slag issuing from a blast-furnace may vary over a range, depending on furnace conditions, but an average value is of the order of  $1400^{\circ}\text{C}$ . The order is, therefore, about that of the  $\alpha \rightarrow \beta$  inversion temperature. However, whatever the method of air-cooling of the slag, the initial cooling to, say,  $1300\text{--}1350^{\circ}\text{C}$ . is probably about the same for all slags and is not unduly rapid. No definite figures can be given on this point, but the general evidence would tend to indicate that the  $2\text{CaO}.\text{SiO}_2$  is in the  $\beta$  condition before final solidification, and, therefore, if other stabilising factors are ignored it might be expected that the  $\beta \rightarrow \gamma$  inversion would take place immediately on passing the inversion point.

This would offer an explanation of the results of Table I. In those dilatometric tests on falling slag in which only a small expansion was measured, it is concluded that the inversion and, therefore, the expansion has already taken place before the test, the visual appearance being a later effect. It follows that the dilatometer test does not provide a suitable routine test of falling.

#### (b) *Liquid-Immersion Tests.*

Certain types of slag are known to disintegrate if immersed in water. This disintegration has been investigated by Guttman<sup>(4)</sup> (*loc. cit.*, p. 58), who has shown it to occur when the slag has a high content of FeO together with a normal amount of combined sulphur. Guttman attributed the disintegration to the hydrolysis of an iron sulphide and described a simple method of testing slags to detect possible disintegration. He termed the disintegration "iron unsoundness" to distinguish it from ordinary falling and his test method consists in a simple immersion of pieces in water.

The content of iron in slags required to produce iron unsoundness is found only very rarely in slags from this country, but the test was applied as a routine measure to those specimens examined for expansion. The spoon sample usually consisted of a fairly glassy outer skin, a more crystalline centre and an intermediate condition between the two. With the large spoon samples of the hematite slags (*e.g.*, B22 and B25) the centre portion was usually falling, while the outside was quite stable. Immersion of these portions

in water did not cause any change. When the intermediate portion was stored in water, it was sometimes found that a breakdown similar to falling took place. These samples had not the high FeO content required for iron unsoundness and the visual appearance of the breakdown was not quite the same. Iron unsoundness shows as a shelling rather like the peeling of layers from an onion; the phenomenon observed was a radial cracking and general crumbling to a powder. It seemed therefore that immersion in water had accelerated the normal falling and that this might provide an accelerated test. Further work was therefore carried out.

To provide reproducible specimens, attempts were first made to prepare slags showing the disintegrating action in the laboratory. By trial a composition was found which when fused in carbon crucibles in a gas furnace showed the ordinary falling phenomena if allowed to cool slowly in the furnace, which was stable if quenched rapidly from  $1450^{\circ}\text{C}$ . by pouring on to a cold plate, but which underwent the water disintegration at a standardised intermediate state of cooling. This latter condition, and the composition chosen, has no very special significance, depending on crucible size, &c., and could no doubt be varied considerably. For record purposes, however, the composition was CaO 51%,  $\text{SiO}_2$  34%,  $\text{Al}_2\text{O}_3$  12% and MgO 3%. The carbon crucibles were of dimension  $2\frac{1}{2}$  in. internal dia. by  $2\frac{1}{2}$  in. deep, and they were closely fitted into fireclay crucibles, covered with a fireclay cap. After heating up, the furnace was maintained for 1 hr. at  $1400^{\circ}\text{C}$ ., the crucibles then being picked out and stood on an iron plate until cold.

The products appeared perfectly stable when stored in air, but broke down on immersion in water. Tests showed also that the slags would break down if immersed in most other liquids. The break-down in benzene and alcohol was as rapid or even more rapid than that in water. With thick liquids, such as liquid paraffin, disintegration was slower, but was brought up to about the same speed as for other liquids when the liquid paraffin was heated to  $50^{\circ}\text{C}$ . or  $100^{\circ}\text{C}$ . and thereby became thinner. The variety of liquids creating the effect indicated that the break-down was not a chemical action. A tentative explanation is that the particular intermediate state of the slag which suffers disintegration is one in which some, but not all, of the  $2\text{CaO}.\text{SiO}_2$  has crystallised, the remainder being in solution in glass. Probably the crystals are smaller than would be formed in normal conditions of cooling and their inversion has caused fine cracks in the structure of the slag. These cracks presumably act as capillaries closed at one end. The structure of the slag is weakened and the building up of air pressure in the capillaries when immersed in liquid is sufficient to complete the crumbling of the slag.

Guttman observed that iron unsoundness in an iron-unsound slag was not manifested when the slag was immersed in aqueous  $\text{NH}_4\text{Cl}$  solution. Similarly the disintegration described above was

inhibited by aqueous  $\text{NH}_4\text{Cl}$  solution, but it was found that this inhibition was associated with the presence in the laboratory slags of traces of sulphide, originating from the carbon crucibles. When special tests were made with slags prepared in crucibles lined with a sulphur-free graphite mixture, a product was obtained which disintegrated in  $\text{NH}_4\text{Cl}$  solution as well as in water. The amount of sulphur required for the inhibition was quite small, about 0.16% of sulphide sulphur and 0.24% total sulphur; the specially prepared slags contained 0.06% of sulphide sulphur and 0.09% of total sulphur.

A further tentative explanation is that polysulphides are formed in the  $\text{NH}_4\text{Cl}$  solution which in some way prevent the passage of liquids into the capillaries, possibly by formation of polysulphide films on the entrances which effectively block the capillaries.

The observations described above were all made either on slags made in the laboratory or on spoon samples. When samples from slags cooled in the ordinary way were investigated only one sample was found of a slag which was stable in air but disintegrated in water in a manner similar to falling. It is concluded therefore that the immersion test is not one which could be applied as a reliable accelerated test of falling. However, this peculiar metastable condition can arise and precautions are necessary. It happens that a water immersion test on slag aggregate is necessary to provide a safeguard against iron unsoundness, so that the one test covers both purposes, though still leaving further tests to be required for falling.

### (c) *The Ultraviolet-Lamp Test.*

During a survey of slag production, a large number of slag samples were secured, representing a characteristic range of those in use in England and Wales, together also with samples of falling slags which had been taken for the examination of methods of test for falling. All of these samples were examined under the ultraviolet lamp, as a routine measure. Under the conditions of the test, sound slags are held to give a violet fluorescence and falling slags to show yellow fluorescent flecks or patches on a violet background. The standard against which the results of the tests were judged was the expert opinion of the ironworks officials on whether a slag was sound, fair, doubtful or falling. The description "fair" applies to certain old bank or pit slags, in which, of course, it is not possible to apply as firm a description as that of a single ball, because more than one ladle of liquid slag may have been involved, while "doubtful" means that it was not certain at the time whether or not the slag would fall.

Of sixty-one samples marked as sound, sixty gave no yellow flecks or patches when exposed under the lamp and one gave a few yellow flecks on a violet background. That is to say, the prediction by the lamp test agreed with the opinion of the manu-

facturers in sixty of sixty-one examples. In the majority of cases, the fluorescent colour was a shade of violet or lilac, but there was a tendency for old bank slags to show only a very dull fluorescence of a dark violet to brown colour. A very glassy slag gave a reddish fluorescence. Glassy spoon samples also exhibited this reddish colour, which is apparently the fluorescent colour of glasses having the chemical composition of slags.

Of the remaining samples, there were twenty-five which were regarded as fair, doubtful or falling at the ironworks. Of these, six were cases of unsoundness due to iron, &c., as detected by their unsoundness in water. They did not show up as unsound under the lamp. The analysis of the remaining nineteen was as follows : Three marked as fair or doubtful were all classified as sound by the lamp test ; eleven of the remaining sixteen marked as falling were classified as unsound by the lamp test, but the other five marked as falling were not satisfactorily classified as such by the lamp test. These last five are set out in detail below :

Sample 62*j*—classified as a quickly falling slag which, at the age of 4 days, showed a considerable amount of powder formation. The lamp test showed no yellow patches.

Sample 65*a*—was a piece of slag which was sound at one end of the piece but powdering at the other. The lamp test showed no yellow patches.

Sample 84*b*—was a piece of fallen slag which had reconsolidated on a bank. The lamp test showed no yellow patches.

Sample 63*b*—was considered to be falling slowly. The lamp test showed only one yellow patch.

Sample 77*c*—was considered to be falling. The lamp test showed only a few isolated yellow patches.

A sample of an efflorescence on a slag gave no particularly significant result under the lamp. Of more importance were tests on five samples of slag concrete, some of which were sound and some had given rise to trouble. The slag in the good concrete showed yellow patches as well as that in the concrete which had failed. Some further examples are required before firm conclusions on the use of the test with slag concrete can be reached, but the present indications are that the test would not be satisfactory for the examination of slag concrete.

Considering only the slag samples on which a definite opinion could be given, it might be assumed that a test which will predict seventy-one out of seventy-seven samples correctly is a reasonably good one. This would undoubtedly be true if the predictions erred on the safe side, *i.e.*, if the errors were all predictions of unsound slags on slags which were classified as sound by experience.



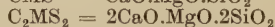
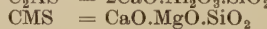
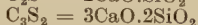
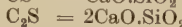
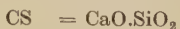
In fact, however, the predictions err in the opposite direction and nearly one-third of the unsound slags are classified as safe.

On the basis of the results obtained, it may be concluded that the ultraviolet-lamp test is not an entirely safe guide to falling slags.

#### 5.—TESTS FOR FALLING SLAG BASED ON SLAG CONSTITUTION.

Analysis of a range of slags from all parts of Great Britain shows the following composition limits of the major constituents: CaO 30–50%, SiO<sub>2</sub> 26–36%, Al<sub>2</sub>O<sub>3</sub> 10–22% and MgO 0–10%. These four constituents make up about 90–95% of the average slag and it is therefore possible to consider slags as compositions in the quaternary system CaO–MgO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>. The phase equilibria in this quaternary system have not been worked out, although the bounding ternary systems and some binary systems within the quaternary system have been determined. The quaternary system as a whole is complicated and within it there must be a number of smaller quaternary systems. An estimation of these has been given by McCaffery,<sup>(6)</sup> who has shown that several smaller quaternary systems may exist within the range of slag compositions. In other words, the compounds formed on complete crystallisation of a slag depend on the smaller quaternary system in which the slag composition falls and slight changes in oxide composition may lead to considerable changes in compound composition. Examples of these changes have been given by McCaffery.

From the point of view of falling slag, only those slags which contain 2CaO.SiO<sub>2</sub> can possibly be of a falling type, that is, if slags crystallise under complete equilibrium, only those compositions falling in quaternary systems in which 2CaO.SiO<sub>2</sub> occurs can give rise to falling. There are three possible quaternary systems in which this can occur in the slag composition range. These systems are: C<sub>2</sub>AS–C<sub>2</sub>MS<sub>2</sub>–CS–C<sub>2</sub>S, C<sub>2</sub>AS–C<sub>2</sub>MS<sub>2</sub>–C<sub>2</sub>S–CMS and MgO–C<sub>2</sub>AS–CMS–C<sub>2</sub>S. It has now become a common practice to use a shorthand notation for the chemical formulæ of the complex silicates and aluminosilicates, especially in phase-equilibrium studies. This notation is used in the present section. The key is :



The notation is not used for the individual oxides, where these occur as compounds. For example MgO is written as such, and not simply as M.

In the very simplest case it would be sufficient to use, as a dividing line between slags which are safe and those which are unsafe against falling, the rule that slag compositions should lie in quaternary systems on the acid side of the three given above.



However, it will be seen later that this would rule out a number of slags as unsafe which are really safe; this simple rule is in fact too conservative. The method based on phase equilibria is capable of more detailed development leading to a closer approximation between theory and the observed conditions of falling.

For simplicity, the development is first applied to a ternary system and then to the quaternary system. The complete equilibria for the ternary system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  have been worked out by Rankin and Wright.<sup>(7)</sup> This ternary system includes a smaller ternary system,  $\text{CS}-\text{C}_2\text{S}-\text{C}_2\text{AS}$ , which is a bounding plane of the

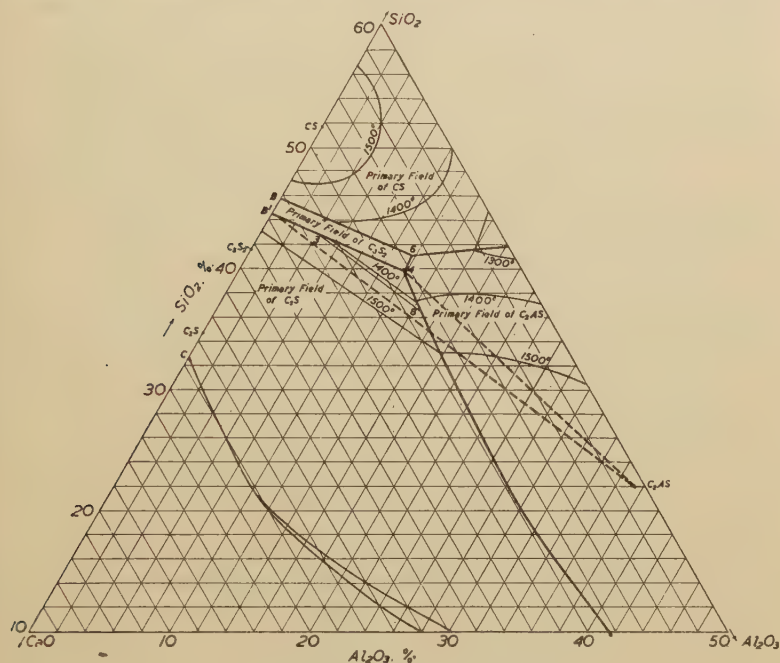


FIG. 2.—System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .

quaternary system  $\text{CS}-\text{C}_2\text{S}-\text{C}_2\text{AS}-\text{C}_2\text{MS}_2$ . The portion of the larger system which includes the smaller is illustrated in Fig. 2, which is a reproduction of part of the Rankin and Wright diagram.

Within this ternary system, if complete equilibrium is maintained, compositions in the triangle bounded by the lines  $\text{CS}-\text{C}_2\text{AS}$ ,  $\text{C}_2\text{AS}-\text{C}_3\text{S}_2$  and  $\text{CS}-\text{C}_3\text{S}_2$  will crystallise to form  $\text{CS}$ ,  $\text{C}_3\text{S}_2$  and  $\text{C}_2\text{AS}$ . Compositions in the triangle bounded by  $\text{C}_2\text{AS}-\text{C}_3\text{S}_2$ ,  $\text{C}_3\text{S}_2-\text{C}_2\text{S}$  and  $\text{C}_2\text{S}-\text{C}_2\text{AS}$  will crystallise to form  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{S}_2$  and  $\text{C}_2\text{AS}$ . The limiting compositions for safety against falling are therefore represented by the line  $\text{C}_2\text{AS}-\text{C}_3\text{S}_2$ , if complete equilibrium is maintained.

It will be observed, however, that  $C_3S_2$  is an incongruently melting compound; its composition falls outside the field in which it is the primary phase, and in consequence the primary field of  $C_2S$  projects into the triangle  $CS-C_3S_2-C_2AS$ . If the crystallisation paths of mixes in this triangle are worked out, it will be found that there are cases where  $C_2S$  crystallises during a part of the cooling range and at a later stage reacts with the residual liquid to disappear again. Referring to Fig. 2, this will happen at some stage of crystallisation of any composition in the area  $C_3S_2-B'-4-C_2AS$ . Compositions falling in the rest of the triangle will never crystallise  $C_2S$  at any stage and the limiting composition line between these two cases is the line  $B'-4-C_2AS$ .

It is unlikely that the cooling conditions of slag are such as to allow true equilibrium to be maintained especially in cases where a solid has to react with a viscous liquid. The chances are therefore that in the region  $C_3S_2-B'-4-C_2AS$ , when once  $C_2S$  has crystallised it will never completely react with the residual melt, but will remain as a solid phase. True equilibrium is then suspended from the point at which the re-solution of  $C_2S$  should begin. This hypothesis of suspended equilibrium has been developed previously for Portland cement clinker equilibrium<sup>(8)</sup> and the argument for it is given in more detail in this previous publication.

Instead then of the line  $C_2AS-C_3S_2$  being the limiting composition line, the line  $B'-4-C_2AS$  becomes the limiting one. The latter is not straight, but forms an angle at the point 4. The range of compositions from  $B'$  to 4 corresponds with  $Al_2O_3$  contents of 0-11.9% respectively. Since the large majority of slags range in  $Al_2O_3$  content from 10 to 22%, the line  $B'-4$  need hardly be considered, except over the range 10-11.9%  $Al_2O_3$ , and if the line  $C_2AS-4$  is projected as far as 10%  $Al_2O_3$  only a very small area of safe slags (in the area enclosed by the projection and the short length of  $B'-4$  from 10 to 11.9%  $Al_2O_3$ ) is ruled out wrongly as unsafe.

By simple co-ordinate geometry it can be shown that the line  $C_2AS-4$  can be converted into an equation :

$$CaO = 1.1SiO_2 + 0.5Al_2O_3 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the actual weight percentages of the oxides should be substituted.

To utilise this equation for slags containing only  $CaO$ ,  $SiO_2$  and  $Al_2O_3$  the value for the right-hand side should be calculated from the analytical data. If this value is less than the actual lime content, then the slag is liable to be of a falling type, but if it is equal to or greater than that for the actual lime content, the slags should be quite safe.

Similar arguments could be applied to the theoretical case of slags containing only  $CaO$ ,  $SiO_2$  and  $MgO$ . The portion of the ternary system  $CaO-SiO_2-MgO$  in which lies the smaller ternary system  $C_2S-CS-C_2MS_2$  (a bounding plane of the quaternary system



$\text{Al}_2\text{O}_3$  region and at high  $\text{MgO}$  contents. Another possible plane is that passing through  $\text{C}_2\text{MS}_2$ - $B'$ - $\text{C}_2\text{AS}$ . This, however, is unsafe in the regions of low  $\text{MgO}$  content. In fact, of course, one flat plane cannot be found to fit the conditions accurately, but an approximation to such a plane is desirable in order to arrive at a simple equation. The two planes given are in the nature of extremes, and by inspection of quaternary models it will be seen that the extremes are not far apart. It is therefore legitimate to find an average plane between the two. Since slag compositions are mainly in the 10–22%  $\text{Al}_2\text{O}_3$  range it is better to weight the average in favour of a plane which is safe over that range, rather than to choose a plane bisecting the angle between the two extreme planes. The choice has therefore been made of a plane passing through

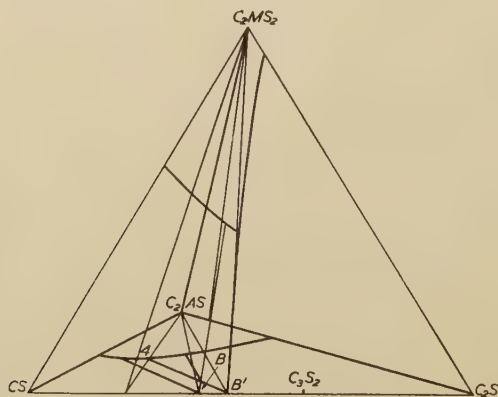


FIG. 4.—Quaternary System  $\text{C}_2\text{MS}_2$ - $\text{C}_2\text{AS}$ - $\text{CS}$ - $\text{C}_2\text{S}$ .

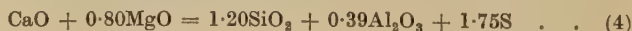
the points  $\text{C}_2\text{AS}$ ,  $\text{C}_2\text{MS}_2$  and the point  $B$  (Fig. 2). Point  $B$  is the eutectic between  $\text{C}_3\text{S}_2$  and  $\text{CS}$  in the  $\text{CS}$ - $\text{C}_2\text{S}$  system.

The equation for this plane is :



Fig. 4, which is a tetrahedral model of the system  $\text{CS}$ - $\text{C}_2\text{S}$ - $\text{C}_2\text{AS}$ - $\text{C}_2\text{MS}_2$  including the experimental details of Figs. 2 and 3, shows the positions of the three planes considered above, the edges of the planes on two of the ternary systems being shown by lines.

Blast-furnace slags contain sulphur, combined as  $\text{CaS}$ . Before applying the equation to a slag it would therefore be necessary to make allowances for the amount of  $\text{CaO}$  quoted in the oxide composition which is present as  $\text{CaS}$ . An allowance can be made directly on the equation which then becomes :





The extent of the experimental determinations of phase equilibria on which the deductions resulting in this formula are based has been outlined in previous paragraphs. Strictly, the only compositions to which it applies are those in the quaternary system  $C_2S$ - $CS$ - $C_2AS$ - $C_2MS_2$ . As the  $MgO$  and  $Al_2O_3$  contents are increased the compositions tend to move out of this system. The prolongation of the plane represented by the equation in the larger system  $CaO$ - $MgO$ - $SiO_2$ - $Al_2O_3$  falls on the safe side of any possible falling composition, however, so that the equation could be used for all slags, with the proviso that it could theoretically exclude some slag compositions which were safe in practice.

It has previously been noted that two other quaternary systems may include  $C_2S$  and hence may give rise to falling slags. These include the compositions at the higher  $MgO$  and  $Al_2O_3$  contents, *i.e.*, those described as  $C_2AS$ - $C_2MS_2$ - $CMS$ - $C_2S$  and  $MgO$ - $CMS$ - $C_2AS$ - $C_2S$ . Phemister<sup>(12)</sup> has recently shown, however, that a mineral, merwinite, occurs in blast-furnace slags. This mineral has the formula  $3CaO.MgO.2SiO_2$  (or  $C_3MS_2$  in the shorthand notation) and Nurse<sup>(14)</sup> has shown it to be an incongruently melting compound. It may, however, occur as a primary phase in the phase equilibrium diagram of  $CaO$ - $MgO$ - $SiO_2$  and  $CaO$ - $MgO$ - $SiO_2$ - $Al_2O_3$ , although it is not shown in Ferguson and Merwin's diagram<sup>(9)</sup> of the  $CaO$ - $MgO$ - $SiO_2$  system; it must almost certainly occur in the final crystallisation in parts of these systems. The effect is that the two sub-quaternary systems mentioned above need further subdivision. Examination of the existing data shows, however, that they are insufficient at present to decide this sub-division with certainty but that a probable division should be to the sub-quaternary systems  $C_2AS$ - $C_2MS_2$ - $C_3MS_2$ - $CMS$ ,  $C_2AS$ - $C_2MS_2$ - $C_3MS_2$ - $C_2S$ ,  $MgO$ - $C_2AS$ - $C_3MS_2$ - $CMS$  and  $MgO$ - $C_2AS$ - $C_3MS_2$ - $C_2S$ . Given complete equilibrium through all stages of cooling,  $C_2S$  would not appear in the final solid state of slags the compositions of which fell within the boundaries of the first or third of these systems. However, since pure merwinite decomposes to  $C_2S$  and liquid on heating, there must, therefore, be a primary field of  $C_2S$  in both systems. It follows that in cooling conditions which do not produce true equilibrium, there is a possibility that  $C_2S$  can persist in parts of the two systems. This situation is not very different from that already discussed in deriving equation (4), except that in this case the experimental data are insufficient to derive a safe plane within the systems which will separate compositions never including  $C_2S$  in their crystallisation paths from those including  $C_2S$  over some portion. If the known data are correct, however, it is possible to derive a plane which is quite certain to be safe. This is the plane passing through  $MgO$ ,  $CMS$ ,  $C_2MS_2$  and  $C_2AS$ . It has the following equation, including the sulphur factor for the same reason as before :

$$CaO = 0.93SiO_2 + 0.55Al_2O_3 + 1.75S \quad . \quad . \quad . \quad (5)$$



The plane represented by equation (5) intersects that represented by equation (4) at the composition line  $C_2AS-C_2MS_2$ . The combined plane  $MgO-C_2AS-C_2MS_2$ -point B (Fig. 2) separates the quaternary system  $CaO-MgO-SiO_2-Al_2O_3$  into two regions, one, on the silica side of the plane, in which compositions can never contain  $C_2S$  at any stage of crystallisation, and one, on the  $CaO$  side, which may crystallise  $C_2S$  at some part of the cooling range. It has to be emphasised that this dividing plane is based on the limited experimental data available and that equation (5) is probably too safe.

However, from the practical point of view it may not be very important to improve on equation (5). The majority of the slag compositions in this country are not affected since their  $MgO$  contents are low enough to bring them within the scope of equation (4). Moreover, an improvement which adjusted the plane to the basic side would mean that the major quaternary system could not be divided up by two planes but, for the purpose of assessing stability, three or more would be required. The gain in accuracy would then be accompanied by an increased complication in calculation.

Using the two derived equations (4) and (5) for assessing freedom or otherwise from falling, the analytical data for the slag under test should be applied to both equations. If the actual value for  $CaO + 0.8MgO$  or for  $CaO$  alone is equal to or less than the values from the summation in the right-hand side of the equations (4) and (5) respectively the slag should be free from falling. The slag should also be free from falling if it satisfies only one of the two equations. It may be expected to be a falling type if it fails to satisfy both equations.

The equations apply best to slags which are cooled slowly, such as slags cooled by the ball method. There is an assumption in equation (4) that slags should not be cooled so very slowly that chemical equilibrium is maintained. The assumption is also made, however, that in silicate systems of this type it is only under very exceptional conditions of cooling that chemical equilibrium can be maintained, especially when the equilibrium requires reaction at invariant points. The slow cooling of the ball method can probably produce equilibrium except for these invariant-point reactions or possibly where equilibrium requires a phase to re-dissolve on cooling.

Slags which are cooled faster than that of the ball method, *e.g.*, by the pit or bank methods, should also be stable if they satisfy one or both of equations (4) and (5), but the more rapid cooling may have the effect of stabilising slags which would otherwise fall if cooled slowly. The use of the equations may therefore reject rapidly cooled slags which are stable in practice. This point is considered in more detail later.

An attempt at experimental verification of the equations has been made. Analysis of all the slag samples obtained in the survey, made by the ball method, which were known by reputation to be

quite free from falling showed that none would have been rejected by application of the formula. In Table II. is given a selection of analytical data for falling slags, or slags on which doubt had been expressed at the ironworks. The CaO data are corrected for the sulphur content of the slag so that it is not necessary to introduce the 1.75S factor into the equations.

TABLE II.—*Application of Equation (4) to Falling Slags.*

Sample No.	CaO. %.	MgO. %.	SiO <sub>2</sub> . %.	Al <sub>2</sub> O <sub>3</sub> . %.	Equation (4).		Safety of Slag Predicted by—	
					CaO + 0.8MgO.	1.20SiO <sub>2</sub> + 0.33Al <sub>2</sub> O <sub>3</sub> .	Equa- tion (4).	Observation at Iron- works.
63B	41.8	3.1	35.0	11.0	44.3	46.3	Safe	Ball slag. Might fall slowly.
64A	41.0	3.2	29.2	14.2	43.6	40.5	Unsafe	Ball slag. Falling.
64E(1)	39.8	5.5	29.2	15.7	44.2	41.3	"	Bank slag. Not falling.
64E(2)	39.0	5.2	27.9	15.5	43.2	39.5	"	" " Falling.
67B	40.6	4.8	31.4	13.7	44.4	43.0	"	Ball slag. Might fall.
67C	40.3	5.4	31.6	13.3	44.6	43.1	"	" " Falling.
70C	39.5	3.1	27.1	19.4	42.0	40.1	"	" " "
75C	41.7	1.8	28.6	20.6	43.1	42.3	"	" " "
77C	41.5	2.2	28.9	19.9	43.3	42.5	"	" " "
79A	43.2	2.5	31.8	18.5	45.2	45.4	Safe	" " Might fall slowly.
88D	41.0	5.6	28.4	16.2	45.5	40.4	Unsafe	Ball slag. Falling.
62A	37.4	4.3	29.7	21.6	40.8	44.8	Safe	" " Not falling.
72D	39.7	3.9	33.1	16.9	42.8	46.3	"	" " " "

\* Analyses by F. J. McConnell, W. G. Grindle and M. W. Miller.

The two slags at the end of Table II. (62A and 72D) illustrate slags which were definitely free from any falling and as such are predicted correctly by the formula. Six of the samples (64A, 67C, 70C, 75C, 77C and 88D) were from slags which had quite obviously fallen, and again are predicted correctly by the formula. Most interest, however, is attached to the remaining five (63B, 64E(1), 64E(2), 67B and 79A); of these, two were of bank slags (64E(1 and 2)). Both of these are predicted by the formula as being of a falling type, and, in fact, one had fallen although the other sample was stable. The reputation of this slag at the works was that if cooled in ladles it tended to be of a falling type. This evidence supports that of the formula. Sample 79A was from a ball slag and it was thought that it might fall slowly. The sample itself has been under observation at the Building Research Station for about eighteen months and has remained stable. The formula predicts stability. It is clear that experience places this slag as a borderline case and it will be observed that the formula does the same; a very slight change in the proportions of the constituents might alter the formula prediction. This example, in fact, gives very good support to the fundamental hypothesis on which the formula is based. Samples 63B and 67B after a similar period had not developed noticeable falling. The formula predicts one as

TABLE III.—*Properties of Slags as Observed and Calculated with Equations (4) and (5).*

Melt No.	Analysis.			Equation (4).		Equation (5).	Predicted by Equations.	Observed.
	CaO.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO + 0.80MgO.	1.20SiO <sub>2</sub> + 0.39Al <sub>2</sub> O <sub>3</sub> .	0.93SiO <sub>2</sub> + 0.55Al <sub>2</sub> O <sub>3</sub> .		
Melts with 5% of MgO.								
1	47.5	38.0	9.5	51.5	49.3	40.5	Falling	Doubtful
2	45.1	40.4	9.5	49.1	52.2	42.8	Stable	Stable
3	42.8	42.8	9.5	46.8	54.4	45.0	"	"
4	40.4	45.1	9.5	44.4	57.7	47.1	"	"
5	49.9	35.6	9.5	53.9	46.4	38.3	Falling	Falling
6	47.5	33.25	14.25	51.5	45.4	38.7	"	"
7	45.1	35.6	14.25	49.1	48.2	40.9	"	"
8	42.75	38.0	14.25	46.75	51.1	43.1	Stable	Stable
9	40.4	40.4	14.25	44.4	54.0	45.4	"	"
10	42.75	33.25	19.0	46.75	47.3	41.4	"	"
11	40.4	35.6	19.0	44.4	50.1	43.6	"	"
12	38.0	38.0	19.0	42.0	53.0	45.8	"	"
13	45.1	30.9	19.0	49.1	44.5	39.2	Falling	Falling
14	45.1	26.1	23.75	49.1	40.5	37.4	"	"
15	42.75	28.5	23.75	46.75	43.4	39.6	"	"
16	40.4	30.9	23.75	44.4	46.3	41.8	Stable	Stable
17	47.5	36.0	11.5	51.5	47.7	38.8	Falling	Falling
18	45.0	33.5	11.5	49.0	50.7	41.1	Stable	Stable
19	42.75	40.75	11.5	46.75	53.4	43.2	"	"
20	41.0	42.5	11.5	45.0	55.5	44.8	"	"
Melts with 7.5% of MgO.								
21	48.5	34.0	10.0	54.5	44.7	37.1	Falling	Falling
22	45.5	37.0	10.0	51.5	48.3	39.9	"	Stable
23	44.5	38.0	10.0	50.5	49.5	40.8	Falling (border-line case)	"
24	42.5	40.0	10.0	48.5	51.9	42.7	Stable	"
25	40.0	42.5	10.0	46.0	54.9	45.0	"	"
26	48.5	29.0	15.0	54.5	40.6	35.3	Falling	Falling
27	44.5	33.0	15.0	50.5	45.4	39.0	"	"
28	42.5	35.0	15.0	48.5	47.8	40.8	Falling (border-line case)	Stable
29	40.0	37.5	15.0	46.0	50.8	43.2	Stable	"
30	48.5	24.0	20.0	54.5	36.6	33.6	Falling	Falling
31	44.5	28.0	20.0	50.5	41.4	37.0	"	Stable
32	42.5	30.0	20.0	48.5	43.8	38.9	"	Falling
33	40.0	32.5	20.0	46.0	46.8	41.2	Stable	Stable
34	38.0	34.5	20.0	44.0	49.2	43.1	"	"
35	44.5	23.0	25.0	50.5	37.3	35.2	Falling	Slight falling
36	42.5	25.0	25.0	48.5	39.7	37.1	"	Doubtful
37	39.5	28.0	25.0	45.5	43.3	39.8	Stable	Stable
38	46.5	34.0	12.0	52.5	45.5	38.2	Falling	Falling
39	44.5	36.0	12.0	50.5	47.9	40.1	"	"
40	42.5	38.0	12.0	48.5	50.3	41.9	Stable	Stable
41	40.5	40.0	12.0	46.5	52.7	43.8	"	"
Melts with 9.0% of MgO.								
42	47.5	31.5	12.0	54.7	42.5	35.9	Falling	Stable
43	45.0	34.0	12.0	52.2	45.5	38.2	"	"
44	42.5	36.5	12.0	49.7	48.5	40.6	"	"
45	40.0	39.0	12.0	47.2	51.5	42.9	Stable	"
46	47.5	28.5	15.0	54.7	40.1	34.8	Falling	Slow falling
47	45.0	31.0	15.0	52.2	43.1	37.1	"	Stable
48	42.5	33.5	15.0	49.7	46.1	39.4	"	"
49	40.0	36.0	15.0	47.2	49.1	41.8	Stable	"
50	45.0	21.0	25.0	52.2	35.0	33.3	Falling	"
51	42.5	23.5	25.0	49.7	38.0	35.7	"	"
52	40.0	26.0	25.0	47.2	41.0	38.0	"	"
53	38.0	28.0	25.0	45.2	43.4	39.8	Stable	"

safe (63*B*), the other as unsafe (67*B*). The formula may therefore err slightly on the side of predicting falling when the slag is really safe.

Further experimental verification of the formula was obtained by laboratory tests. For these, synthetic slag mixes made up from the pure oxides were prepared and melted in carbon crucibles ( $2\frac{3}{8}$  in. internal diameter,  $2\frac{1}{2}$  in. deep) in a gas furnace. After heating to the maximum temperature required for melting, which varied from  $1400^{\circ}$  to  $1500^{\circ}$  C., the mixes were cooled slowly at the rate of  $100^{\circ}$  C. per hr. to  $1200^{\circ}$  C.; the furnace was then shut off, and the mixes allowed to remain in the furnace until it was cold. In practice this meant that the mixes were allowed to remain in the furnace overnight. After cooling, the mixes were inspected to see whether falling had taken place. If no falling was observed, the samples were retained for a few days to observe whether falling developed. The results are given in Table III., together with the values for formulæ (4) and (5).

Of the twenty melts containing 5% of MgO there is agreement between the predicted and observed results in all but No. 1. There is some doubt on the observed result for No. 1, and it may be concluded that the formula is verified for this series. The twenty-one melts containing 7.5% of MgO do not show quite such good agreement. Neglecting the observed result of No. 31 (which was observed to be stable although predicted as falling) because the observed and predicted result of No. 32 agrees, even although the CaO content was lower than that of No. 31, there are three other cases of discrepancies (Nos. 22, 23 and 28) and one case (No. 36) where there was some doubt on the observed condition of the melt. The discrepancies are, however, all on the safe side. The twelve melts containing 9% of MgO only agreed in four cases with the predicted results. In the remaining cases the slag was predicted as unstable when in fact it was stable. These mixes tended to be very difficult to melt under the furnace conditions used. In order to produce complete fusion it was necessary to maintain the furnace at  $1500^{\circ}$  C. for two hours and the subsequent rate of cooling was arranged so that the temperature was lowered to  $1150^{\circ}$  C. during a 4-hr. period. The conditions were therefore not exactly similar to the other series. By "complete fusion" in these series is meant that the melts had settled to a solid button at the bottom of the crucibles when they were observed after cooling. It is, of course, quite possible that, with this crude method of observation, some of the melts might not have been completely liquefied.

It is clear that, from the laboratory tests, the formulæ are most accurate at low MgO contents and that above 7.5% of MgO they lose accuracy. However, they have the advantage that the tendency is to predict a stable slag as falling rather than to predict a falling slag as stable. This introduces an element of safety in using the tests for determining whether a slag will be suitable as a concrete or road aggregate.



An observation frequently made in blast-furnace practice is that falling slags can often be changed to stable types by substituting dolomitic limestones for part of the furnace burden in place of calcareous limestones. The effect is to substitute part of the CaO in the slag by MgO. The formula (5) has an interest in providing a fundamental background for this. If the MgO content of the slag is great enough to move the composition into one of the high-MgO quaternary systems, equation (5) is the most suitable for use in predicting falling. This formula does not include MgO in either side of the equation. Since the CaO alone has to be taken into account and the CaO content is lowered through the dolomite in the burden, the slag may be stabilised. However, if insufficient dolomite is used, so that the composition of the slag remains in the quaternary system for which equation (4) applies, then the MgO has only a negligible effect in stabilising the slag, because in equation (4) 0.8 times the MgO content must be taken into account along with the CaO.

Dolomite additions will not necessarily prevent falling altogether; in the practical case mentioned earlier of a high-MgO slag, the latter was frequently of a falling type. However, in practice the effect of dolomite seems to be greater than would be estimated by the formula. An indication of this is shown in Table III. where the high-MgO laboratory slags were more stable than was predicted. This is a feature which could be expected from the argument given earlier, on which equation (5) was developed.

The use of the formula for control purposes in a works, to avoid storing unsuitable slag balls longer than is absolutely necessary, raises the problem of slag analysis. It is not the practice to analyse every slag ladle run from the furnace. In most works a combined sample from the day's output of slag from a furnace is analysed overnight for CaO and SiO<sub>2</sub> and, in some works, for total sulphur. Periodically a check complete analysis is carried out. The routine daily data are, therefore, insufficient for a daily estimation of falling. However, it happens that the contents of MgO and Al<sub>2</sub>O<sub>3</sub> are probably more constant during the steady operation of one furnace than the contents of CaO and SiO<sub>2</sub>. Moreover, the content of MgO is usually relatively low, while the factor of 0.39 for Al<sub>2</sub>O<sub>3</sub> in the formula means that small changes in the Al<sub>2</sub>O<sub>3</sub> content affect falling less than similar small changes in the other constituents. This suggests that as a routine control between the periods of complete analysis, it may be possible to apply constant factors in the formula instead of the MgO and Al<sub>2</sub>O<sub>3</sub> values. For example, the formula for equation (4) might be reduced for control purposes to  $\text{CaO} = 1.20 \text{ SiO}_2 + K$ . A slag which had an Al<sub>2</sub>O<sub>3</sub> content of 18% and an MgO content of 3% would have a control equation of  $\text{CaO} = 1.20 \text{ SiO}_2 + 4.6$ .

A reference has been made earlier to a suggestion that the limiting composition should be determined by the ratio  $\text{CaO/SiO}_2 =$



1.3, or  $\text{CaO} = 1.3 \text{ SiO}_2$ . It will be observed that the present suggestion of a formula  $\text{CaO} = 1.20 \text{ SiO}_2 + K$  for any one furnace is a modification of the earlier suggestion. The two formulæ will only agree when  $0.1 \text{ SiO}_2 = K$ . For the majority of slag compositions in Great Britain,  $K$  is slightly greater than  $0.1 \text{ SiO}_2$  and the effect is to predict slags as stable which contain 1–2% more CaO than the limit set by the earlier formula. There are, however, a few cases in which the new formula would set a limit at a lower CaO content than that of the older formula.

## 6.—TESTS FOR FALLING SLAG BASED ON OBSERVATIONS UNDER THE MICROSCOPE.

The influence of rapid cooling in stabilising slags against falling, such as by pouring the molten slags on banks or in pits may be due

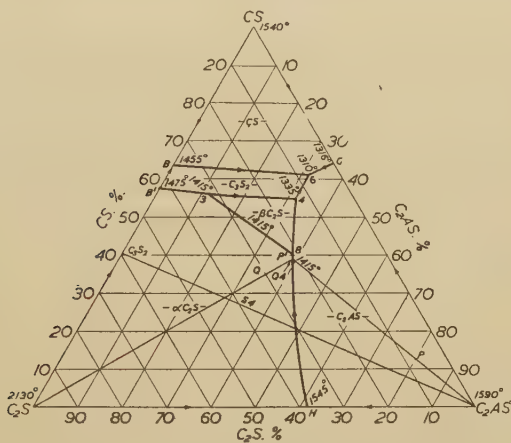


FIG. 5.—Ternary System CS- $\text{C}_2\text{S}$ - $\text{C}_2\text{AS}$ .

either to failure of the  $2\text{CaO}.\text{SiO}_2$  to crystallise and its being retained in solution in a glass, or to some stabilising influence of the glass formed around the crystals, in the same way as  $\text{B}_2\text{O}_3$  seems to bring about stabilisation. This effect may be illustrated by reference to Fig. 5, the ternary system CS- $\text{C}_2\text{S}$ - $\text{C}_2\text{AS}$ . A slag having a composition  $P$  ( $\text{C}_2\text{AS}$  80%, CS 13%,  $\text{C}_2\text{S}$  7%) in the area  $\text{C}_2\text{AS}-\text{C}_3\text{S}_2-\text{B}'-4$ , will first begin to crystallise  $\text{C}_2\text{AS}$  at about  $1552^\circ \text{C}$ . on cooling.  $\text{C}_2\text{AS}$  will continue to crystallise until the liquidus composition reaches  $P'$ , at  $1439^\circ \text{C}$ . At this point 67.13% of solid will have crystallised and 32.87% of molten liquid will be left. If the material is quenched at this point, the liquid will become a glass and no  $\text{C}_2\text{S}$  will appear. The resulting slag should be stable. If,

however, cooling continues slowly beyond  $P'$ ,  $C_2AS + C_2S$  will crystallise together while the composition of the liquidus changes along  $P'-4$ . At 4 the composition will be  $C_2AS$  72.44%,  $C_2S$  3.81% and liquid 23.75%. On further cooling, a reaction should take place at 4 and after the reaction the composition should be  $C_2AS$  74.13%,  $C_3S_2$  7.87% and liquid 18.0%. The subsequent course of the liquidus is along 4-6. With complete equilibrium, the mix would become entirely solid at point 6, with a composition  $C_2AS$  80%,  $C_3S_2$  11.72%,  $CS$  8.28%, but if the equilibrium is frozen the reaction at point 4 does not take place. It is possible that the glass films round the  $2CaO.SiO_2$  grains might cause the crystalline inversion to be inhibited but practical data on this are lacking.

The same course of crystallisation up to point 4 would take place for mixes in the  $C_2AS$  primary field in the  $C_3S_2-C_2S-C_2AS$  triangle, but in general less  $C_2AS$  and more  $C_2S$  would be formed and there would be no reaction at point 4; the mixes would go entirely solid at this point.

A mix of composition point  $Q$  would first crystallise  $C_2S$ , and, whatever cooling method was adopted,  $C_2S$  would appear in the final material, unless of course the quenching was such as to produce 100% glass.

To sum up, the formula method of the preceding section would prevent the use of any melt on the high-lime side of the line  $C_2AS-B$ , yet, by suitable rapid cooling it is theoretically possible to produce slags on the high-lime side of this line which would not fall. This can be said almost with certainty of mixes where the quenching retains the  $C_2S$  in solution in the glass. It may be that even if a small amount of  $C_2S$  is formed the slag will not fall owing to the  $C_2S$  being stabilised by the glass, but there is no experimental evidence on the point and it is therefore necessary, for safety, to disregard it.

Any experimental method which could show that no crystalline  $C_2S$  was present in a slag would justify a conclusion that the slag was safe; a method which showed  $C_2S$  to be present would justify a conclusion that the slag might be unsafe. Two possible methods are microscopic examination and X-ray analysis. The latter, however, is probably not sensitive enough for detecting small quantities of the material and moreover is a somewhat too specialised technique for use as a routine test method. Microscopic methods on the other hand have long been well-established features of iron- and steel-works laboratory control.

Previous workers have described investigations on the micro-structure of slag, particularly in relation to falling.\* In examining slags under the microscope in the present investigation it was natural to use first the method of examining thin sections by transmitted light, as is used for rock sections and as was used in the

\* For example, E. Hollmann,<sup>(10)</sup> K. Endell<sup>(11)</sup> and A. Guttman<sup>(4)</sup> (*loc. cit.*, pp. 42-53).

previous investigations. The technique enables the general structure of the slag to be observed, and, once the optical properties of the minerals to be expected are known, the more important of them can be identified. As examples of slag structure, Fig. 6 illustrates the appearance of a glassy slag, Fig. 7 a slag which is still glassy but in which more crystallisation has taken place than in Fig. 6, while Fig. 8 shows a fairly completely crystallised slag. The general structure of a slag as observed under the microscope depends not only on its chemical composition but also on the way in which it has been cooled. Thus a slag in the range of high lime and alumina content may show large and well developed crystals when cooled slowly in the slag ladles, but smaller crystals and less complete crystallisation when cooled by pouring in pits or on a bank. A more siliceous slag may exhibit the second type of structure even when cooled slowly in the ladle. The elongated crystals in Fig. 8 are those of melilite, the solid solution of gehlenite ( $C_2AS$ ) and akermanite ( $C_2MS_2$ ). Melilite crystals make up the greater part of the structure of practically all the slags examined in the present investigation. They appear as crystals of rectangular outline with cleavages parallel to the edges. The properties determined are: Uniaxial negative, medium birefringence, refractive index about 1.65. In some slags the crystals show an elongated form and are comparatively clear, in others the form is more tabular and the crystals contain opaque inclusions in the form of a Maltese cross. Zoning at the edges is common, as would be expected when a solid solution is crystallising from a melt.

The next most frequently occurring constituent is pseudo-wollastonite,  $\alpha$   $CaO.SiO_2$  (Fig. 9). This is found as prisms or needles with refractive indices  $\alpha = 1.609$ ,  $\gamma = 1.650$ . It is almost uniaxial, optical character positive, and often occurs as simple twins with  $5^\circ$  between the extinction positions. It is found chiefly in the interstitial material between the melilite masses.

Merwinite ( $3CaO.MgO.2SiO_2$ ) is also sometimes observed. In those slags available to the Building Research Station, this mineral has only been found in some of the slags having an  $MgO$  content greater than 5%. Its appearance and optical properties have recently been described by Phemister,<sup>(12)</sup> who was good enough to verify the mineral in the Building Research Station collection. It occurs either as long needles or tabular masses and is characterised by high refractive indices ( $\alpha = 1.705$ ,  $\gamma = 1.715$  in slags;  $\alpha = 1.708$ ,  $\gamma = 1.718$  in the pure compound), a characteristic polysynthetic twinning, biaxial, with optical character positive. The optic axial angle is given by Phemister as  $2V = \text{about } 70^\circ$ .

Merwinite and pseudo-wollastonite do not occur together in slags. This can be foreseen from an examination of the phase-equilibrium diagrams. The merwinite is, however, sometimes associated with  $2CaO.SiO_2$ . The latter can also occur without associated merwinite either in the matrix or as inclusions in the melilite.

$2\text{CaO}.\text{SiO}_2$  has the form of rounded, transparent grains, which are biaxial with a refractive index of about 1.7 and a high birefringence. The crystals often show a parallel cleavage and the optical character is sometimes positive and sometimes negative. Illustrations of the appearance under the microscope are shown in Fig. 10. The change in optical sign is probably dependent on whether the compound is in the  $\beta$  or the  $\gamma$  form. The refractive indices of pure  $\beta$   $2\text{CaO}.\text{SiO}_2$  are  $\alpha = 1.715$ ,  $\gamma = 1.735$ ; those of  $\gamma$   $2\text{CaO}.\text{SiO}_2$  are  $\alpha = 1.642$ ,  $\gamma = 1.654$ . There are occasions, however, when the  $\gamma$   $2\text{CaO}.\text{SiO}_2$  in the slags retains the higher index of 1.7. This has also been observed occasionally in quenching experiments on the pure materials, and it is thought that there may be an intermediate stage in the inversion of  $\beta$  to  $\gamma$  at which all or most of the crystal properties change, but the refractive index as determined by the immersion method is either unchanged or only slightly reduced.

A fourth constituent which is found dispersed through most sections of slag consists of rounded semi-opaque grains of very high refractive index. The grains are usually assembled in patterns. These have been identified by Guttman as calcium sulphide. Although no systematic measurement has been made of the quantity of calcium sulphide present, observation of a large number of sections gave the general impression that in well-crystallised slags, *i.e.*, the higher-limed type which had been cooled slowly, more calcium sulphide crystals were visible than in the structures showing smaller crystals and more glass, even when analysis showed the quantity of sulphide to be approximately the same. The inference is that in the more glassy structures, some of the sulphide may be in the glass or appearing as fine-grained crystals associated with the ground mass. Other constituents found occasionally in the ground mass are brown pleochroic feathery growths and black opaque material. The former is possibly an iron or manganese compound and the latter magnetite. In one slag crystals of spinel were noted.

McCaffery <sup>(6)</sup> has described a compound called "madisonite," with the formula  $2\text{CaO}.2\text{MgO}.\text{Al}_2\text{O}_3.3\text{SiO}_2$  which, if it exists, may be expected to occur in some slags. However, those slags which are of interest as being in the region of falling slags are not likely to contain madisonite, which would only be expected in more acid slags, possibly in those types in which anorthite ( $\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$ ) or diopside ( $\text{CaO}.\text{MgO}.2\text{SiO}_2$ ) might occur. As a matter of interest, mixed oxides of the madisonite composition were fused together and crystallised. The product appeared to be homogeneous under the microscope, and a heating curve on it gave a single thermal arrest at  $1385 \pm 5^\circ \text{C}$ . This appears consistent with compound formation, but could also apply to a solid solution in which the liquidus and solidus temperatures are not very far apart. The optical properties determined on the crystals were: Refractive indices,  $\alpha = 1.661$ ,  $\beta = 1.669$ ,  $\gamma = 1.686$ ; optical character, positive;



optic axial angle,  $2V = 60 \pm 5^\circ$ ; extinction angle (maximum),  $42^\circ$ ; cleavage parallel to the prism axis. These properties accord well with those of the monoclinic pyroxene series, with diopside ( $\text{CaO.MgO.2SiO}_2$ ) as the end member of the solid solution series. While the evidence is not conclusive, it appears that the madisonite composition is more likely to be simply a point in a pyroxene solid solution than a distinct quaternary compound.

After some experience in the examination of slag sections by this method, it should be possible to give a reasonable opinion whether  $2\text{CaO.SiO}_2$  is present in a slag or not, but it may often be found difficult to decide the point with absolute certainty, when only a small amount of  $2\text{CaO.SiO}_2$  is present in association with other crystals in the matrix.

In an attempt to find better microscope methods, attention was directed to the possibilities of methods using polished sections examined by reflected light. Recently this method has been revived for the examination of Portland cement clinker and it has been shown<sup>(13)</sup> that there are etch reagents which will etch many of the constituents of Portland cement clinker specifically. The specific reagent for  $\text{C}_2\text{S}$  in clinker is hydrofluoric acid vapour, which etches  $\text{C}_2\text{S}$  to a blue colour, leaving the other reagents as a grey or brown background.

Polished specimens have been prepared from the slag specimens. In the first attempts, the same methods of polishing were tried as have been described previously for Portland cement,<sup>(13)</sup> making use of slow-speed laps. While this method produces very good specimens, it has been found for slags to be unnecessarily cautious; high-speed laps can be used quite successfully. The method finally adopted is as follows:

Slags usually contain pores and the first step is therefore to impregnate them with resin. The piece of slag, of about  $\frac{1}{2}$  in. size, is placed in a glass specimen tube in a desiccator fitted with a two-holed rubber bung in the cap, through one hole of which a separating funnel or flask fitted with a tap is inserted, the other being used for evacuating. The desiccator is held evacuated for 2 hr. and then resin (Bakelite R0014) is run on to the specimen, slowly by means of the dropping funnel, until the specimen is covered. The vacuum is held for a further period and the specimen tube and contents then removed and heated in an oven for 4 hr. at  $50^\circ \text{C.}$ , followed by 24 hr. at  $100^\circ \text{C.}$  in order to harden the resin. Several specimens can, of course, be prepared at one time in this part of the process.

The hardened resin, which now contains the slag specimen, is removed from the specimen tube for the grinding operation.

A polished surface on the slag specimen is produced by means of the following grinding operations, taken in succession:

- (1) On a rotating steel lap with 120 carborundum and water.

- (2) By hand, on a glass plate with 220 carborundum and water.
- (3) By hand, on a glass plate with 4F carborundum and water.
- (4) On a rotating cloth-covered lap, using "Sira" abrasive, grade A.
- (5) On a rotating cloth-covered lap, using one lot of rouge and water, and polishing until dry.

If the specimen is examined under the microscope, its surface will be found not to reflect as highly as a metal specimen, but it should be scratch-free and may show slight differences in shades over its surface owing to the difference in reflection from the different constituents. The CaS will show as a whiter constituent than the others, as is illustrated in Fig. 11.

For more complete observation of the structure the surface requires to be etched. In searching for a simple test for  $C_2S$ , however, it is unnecessary to consider etching the whole structure if a reagent can be found which etches only the  $C_2S$ . In fact a specific reagent of this type has obvious advantages for routine purposes. In the first experiments the hydrofluoric acid vapour reagent which had proved specific for  $C_2S$  in Portland cements was used. It was found to act with the  $C_2S$  in slags, but also etched some of the other constituents. An etch which is used as a general reagent for Portland cement was then tried, namely a  $\frac{1}{4}\%$  solution of  $HNO_3$  in absolute alcohol. This etch was much more suitable, and, for low-MgO slags, appeared to etch only the  $C_2S$  and the CaS, except for a light background etching. With higher MgO contents, however, another constituent was etched as well, and this sometimes led to confusion. This other constituent was found to be merwinite.

It should be mentioned that these tests were made on slags which had been first examined carefully in thin section, only those which definitely contained  $C_2S$ , or in which  $C_2S$  was definitely absent, being chosen.

After a search for more suitable reagents, one was finally found in a solution of  $MgSO_4$  in water. The reason which led to suggesting this reagent was that there was a possibility that  $C_2S$ , the most basic compound present, might be attacked through one of the CaO molecules in its composition. In the Portland cement investigation the reagent which is normally used for free lime determinations, *e.g.*, ethylene-glycol, was found to give a more or less specific etch for the most basic silicate,  $3CaO \cdot SiO_2$ .  $MgSO_4$  solution, in that investigation, was found to have this effect but tended to etch the  $C_2S$  also. In the slag investigation it was not necessary to take account of  $3CaO \cdot SiO_2$ , which does not occur in blast-furnace slags, and it seemed possible that, given longer periods for reaction, or using more intensive conditions, such as hot or concentrated solutions, the  $C_2S$  would be sufficiently attacked. Ethylene-glycol

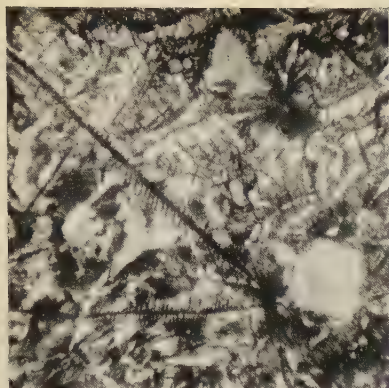


FIG. 6.—Glassy Slag. Transmitted light.  $\times 400$ .

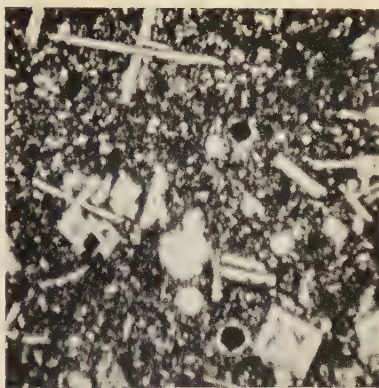


FIG. 7.—Glassy Slag, partly crystallised.  $\times 400$ .



FIG. 8.—Slag showing Elongated Melilite.  $\times 400$ .

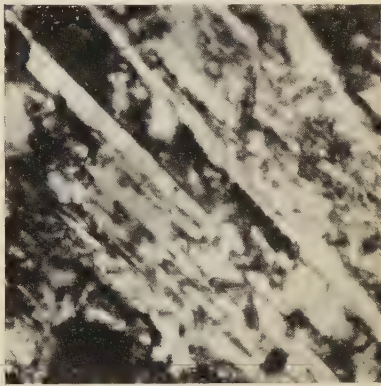


FIG. 9.—Pseudo-Wollastonite in Slag. Ordinary light.  $\times 600$ .

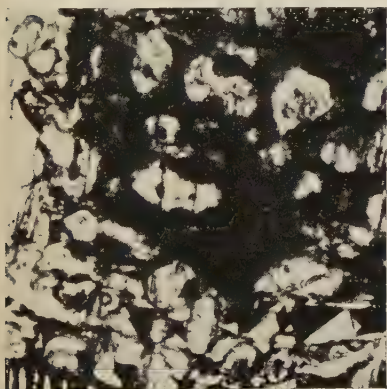


FIG. 10.—Calcium Orthosilicate in Slag.  $\times 600$ .

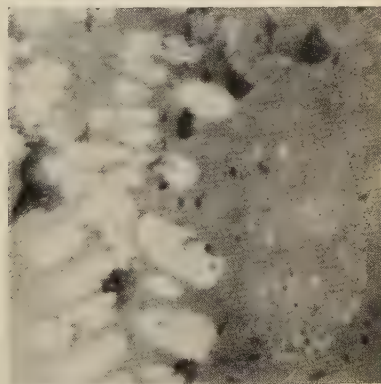


FIG. 11.—Calcium Sulphide in Slag. Polished section, unetched.  $\times 360$ .

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[To face p. 48 P.]



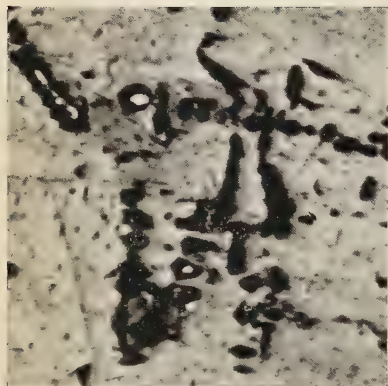


FIG. 12.—Calcium Sulphide in Slag. Polished section, etched with 1% nitric acid in alcohol (3 sec.).  $\times 120$ .

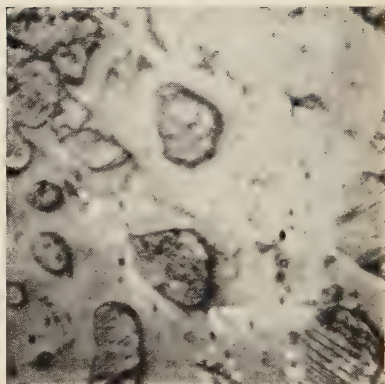


FIG. 13.—Calcium Orthosilicate in Slag. Polished section, etched with 1% nitric acid in alcohol (3 sec.).  $\times 360$ .

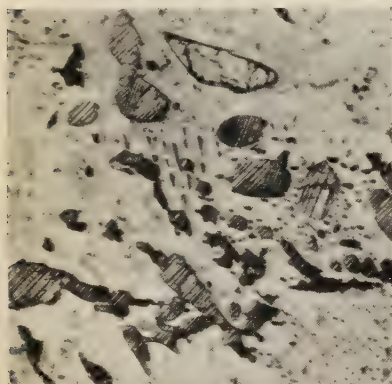


FIG. 14.—Calcium Orthosilicate in Slag. Polished section, etched with magnesium sulphate solution.  $\times 120$ .

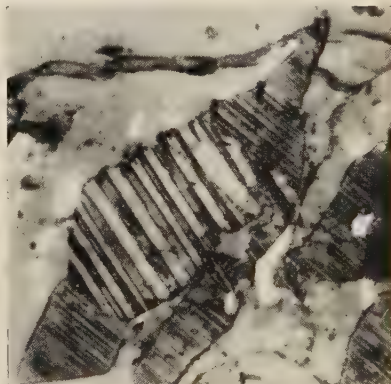


FIG. 15.—Calcium Orthosilicate in Slag. Polished section, etched with magnesium sulphate solution.  $\times 540$ .



gave negative results, but 10%  $\text{MgSO}_4$  solution, used hot ( $50^\circ \text{C.}$ ), etched the orthosilicate strongly, the rest of the structure being only faintly etched. Even the  $\text{CaS}$  was usually not etched with this reagent; it retained its unetched, white, highly reflecting appearance.

The method of etching is to pour the etching solution, previously heated to  $50^\circ \text{C.}$ , into a clock glass; to immerse the specimen, polished face downwards, in the solution for one minute, rocking the glass slightly during the etch period; to remove the specimen and wash it by immersing in water; and, finally, to dry it by careful dabbing on lens-cleaning tissue or other similar paper. Care is required in drying, to avoid destroying the clean outline of the etch.

The specimen is examined under reflected light, using magnifications successively of about 120 and about 360 diameters.

The results produced by these methods are illustrated by Figs. 12-15.

Fig. 12 shows a slag which is perfectly stable, after etching with the  $\text{HNO}_3$  etch. The black material in the form of a pattern of circular or oval grains is  $\text{CaS}$ . Fig. 13 is a section from a falling slag, etched with the  $\text{HNO}_3$  reagent. The circular grains of  $\text{C}_2\text{S}$  are to be observed, some of them having parallel striations across the surface. This is a specimen from the same slag as was illustrated in thin section in Fig. 10. Fig. 14 is of a falling slag etched by the  $\text{MgSO}_4$  reagent. It shows the circular grains with parallel or cross-hatched striations of  $\text{C}_2\text{S}$ . Fig. 15 is of another slag containing  $\text{C}_2\text{S}$ , the etched crystals being shown at higher magnification, the parallel striations again showing.

Tests have been made on slags which in practice are cooled by the pit method to stabilise them because they normally or frequently fall if cooled more slowly. None of the pit slag specimens showed evidence of  $\text{C}_2\text{S}$  under the etch tests. All the falling slags examined showed the  $\text{C}_2\text{S}$  etch reaction. In addition some of the slags of which the stability was doubtful showed the  $\text{C}_2\text{S}$  etch reaction.

It is concluded, therefore, that this test is also slightly on the safe side in the sense that it may exclude a few slags which are safe in practice. This is particularly so if the criterion of the test is simply one of etching or not etching. If etching takes place and the etched grains show parallel striations it seems almost certain that the specimen is falling or is from a slag in which part is falling.

It may be worth reiterating that the effect of the formula and microscope test is to exclude any slag which contains crystalline  $2\text{CaO} \cdot \text{SiO}_2$ , whether or not the latter has remained metastable in one of the high-temperature forms when cold. It may be that the high-temperature forms can be retained without change by some stabilising effect, but as nothing is known about this experimentally, it cannot be taken into account at present.

## 7.—CONCLUSIONS.

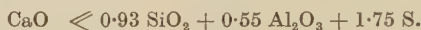
An investigation on the stability of air-cooled blast-furnace slag has led to the following results :

(a) Tests based on measurement of volume change have not proved satisfactory for determining whether or not a slag will fall.

(b) The water-immersion test, which must in any event be used to test for "iron unsoundness," may also accelerate falling in a few instances and therefore provides a partial test for falling.

(c) The ultraviolet-lamp test tends to err on the unsafe side in detecting falling slags. Tests (d) and (e) err on the safe side.

(d) A slag is safe from falling if its percentage weight composition is such that it conforms to one or both of the following conditions :



(e) Slags are safe even if they do not comply with the requirement of (d) above if they show no  $2\text{CaO} \cdot \text{SiO}_2$  etch reaction when polished sections etched by 10% hot aqueous  $\text{MgSO}_4$  solution are examined by reflected light under the microscope. This condition is found in some slags cooled by methods which lead to more rapid chilling than the "ball" method.

(f) Since test (e) over-rides test (d) the latter may be thought to be unnecessary. However, slags are analysed in the normal course of blast-furnace operation and test (d) only requires a calculation from this analysis. If the slag is shown to be safe by this test it is not necessary to carry out the more complicated operations of test (e); test (d) therefore has advantages in convenience.

## ACKNOWLEDGMENTS.

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# THE PRODUCTION IN ROTARY FURNACES OF STEEL FOR CASTINGS.\*

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(Figs. 1 to 8 = Plates III. and IV.)

## SUMMARY.

The manufacture of plain carbon steel in 5-ton Sesci rotary furnaces is described. The furnaces use monolithic acid refractory linings of British origin, and are fired with pulverised coal. The charge consists of 98.5% of railway spring and tyre scrap with not more than 1.5% of pig iron. After numerous experiments the procedure is now to boil, work down and finish in a normal way, though ore additions are seldom required. Details are given of the properties of the resulting steel and slag, and the working data are compared with those of a 35-ton fixed acid furnace.

Great difficulties were encountered in securing a good life from the refractory linings. With intermittent working this has been raised from a beginning of 29 heats per lining to an average of 125, with a record value of 226. A daily patching technique, developed to enable improved life to be obtained, is described. Chemical, physical and petrographical data of patch and various lining materials are given. It has been found that the most useful lining is one with adequate refractoriness and low after-expansion, but, above all, a facility for forming a durable ceramic bond with the patch repair.

## (1) *Introduction.*

It appears that a manufacturer of railway material was the first worker in ferrous metallurgy to make a practical success of rotary furnaces. At the Cincinnati Railway Works in 1868, S. Danks produced wrought iron for rails in a large coal-fired refractory-lined drum, which rotated about a horizontal axis and rested upon permanent bearings. The basic lining of powdered iron ore and lime was applied as a paste in sections, and afterwards dried and heated. Patches were then melted in turn so as to produce a liquid pool, into which lumps of ore were thrown to chill and solidify the fettling. The present paper outlines the production of steel at Crewe Locomotive Works in a Sesci furnace something like that of Danks, but operating with an acid lining at temperatures nearly 500° C. higher than his.

The history of the development of rotary puddling furnaces is not without interest, and from Desch's<sup>(1)</sup> review of the subject we

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† Lately of London, Midland and Scottish Railway Company's Locomotive Works, Crewe.

learn that in 1853 Walker and Warren at Dowlais operated  $\frac{1}{2}$ -cwt. charges in a cylindrical machine which rotated about a horizontal axis. Tooth, in 1859, designed a furnace with a movable flue serving as a door, the lining being of fireclay and not devoid of trouble. Menelaus<sup>(2)</sup> made many experiments with rotary furnaces and always had trouble with the linings, his first choice of ganister being later replaced by rammed titaniferous iron ore from Norway.

Danks appears practically to have overcome the difficulties of construction and refractory lining, but interest in his undertaking evaporated, owing to the contemporary development of steel-making by the Bessemer and open-hearth processes. Two rotary puddling furnaces operated in Italy in recent years, and during 1918 research in France was directed to producing pig iron in a rotary furnace, using pulverised coal as a fuel. Amongst others, the Sesci furnace was thus developed for melting iron for foundry purposes, and during 1932 Messrs. Armstrong Whitworth at Gateshead-on-Tyne made steel in a plant of this type installed in their iron foundry, and similar work was carried out in Germany.<sup>(3)</sup> About the same time the Mons Steel Foundry in Belgium operated Sesci furnaces entirely for steelmaking,<sup>(4)</sup> and the Aktiebolaget Bofors in Sweden have used rotary plant extensively for steel production.

## (2) *Choice of Process.*

For many years the L.M.S. Railway Company has aimed at the utilisation of the maximum amount of its own scrap in its internal metallurgical processes, and has simultaneously obtained satisfactory results with pulverised-coal-fired installations. For the manufacture of steel castings a Tropenas converter plant and a 12-ton acid open-hearth plant had hitherto been employed, but the claims of the Sesci process as a substitute for these were put before Mr. W. A. Stanier, Chief Mechanical Engineer, by Mr. E. Millington, then Chief Metallurgist. The electric arc and the open-hearth processes with acid or basic linings were also considered, but the method which normally used the minimum amount of pig iron appeared particularly attractive. Since it was claimed for the pulverised-coal-fired rotary furnace that the high working temperature available would give very fluid metal, heat from exothermic bath reactions due to the oxidation of pig iron could be dispensed with. The decision was made about 1932 to instal two Sesci furnaces, the ultimate aim being to develop a melting-down technique analogous to the crucible process. As is well known, this requires neither pig iron nor a boiling procedure, and generally relies for the production of killed steel on the content of manganese. That the Sesci steelmaking process had hitherto worked only with an acid lining was offset by the circumstance that good railway scrap low in sulphur and phosphorus was available, and it was hoped that if necessary a basic lining might ultimately be used. Besides the

reduced consumption of pig iron, the advantage of the rotary-hearth furnace over the Tropenas converter lies in the better control of the steelmaking process and the avoidance of any metal loss by projection. Adjustment of the pulverised-coal distributor and the positive air blower should produce either oxidising or reducing flames as required, whilst the temperature and composition control is much more flexible than in the converter. It is a disadvantage that, owing to the absence of side doors, the Sesci bath can be observed only by stopping the flame and sliding back the movable exhaust head, and, above all, the maintenance of the lining presents considerable difficulties.

### (3) *Description of the Plant.*

The 5-ton non-reversing furnace made under the Sesci-Garreau patents and illustrated in Fig. 1 consists of a horizontal cylindrical barrel about 10 ft. long and 7 ft. 8 in. in external and 5 ft. 2 in. in internal diameter, terminating at each end in a truncated cone to give an overall external length of about 15 ft. 4 in. It is built of boiler plate with heavy reinforcements. No special provision is made in the steel structure for expansion effects, and the linings must therefore have only slight after-expansion. One end of the furnace is fitted with a mixing chamber and the Sesci coal burner. The exhaust gases escape from the other into a movable head leading by a downcomer to a metallic recuperator of special design. A by-pass is provided so that any proportion of the hot gases can go direct to the chimney, and by this regulation the combustion air is preheated to within limits of 400° to 600° C., as temperatures above 600° C. would cause combustion in the mixer and destroy the grid. The movable head may be displaced in a direction at right angles to the furnace axis, so as to permit of charging and sampling. The barrel is fitted with two cast-iron pathways running on four sets of double rollers, and a 7½-h.p. motor with reduction gear and push button control drives a sprocket chain wound round the barrel, which enables complete rotation of the furnace to be made in both directions, with automatic reversal. Alternatively, a slow rotation in the tapping direction with a fast return or a partial rotation in either direction can be obtained. The original chain drive has been moved to the outlet end of the barrel, as it is cooler in this position. Diametrically opposed tapping spouts are provided at the middle of the barrel.

The fuel supply consists in the first place of a bituminous coal of about 30% volatile matter content, which from the pulveriser passes to a hopper and a variable output feeder and is thence blown through the mixer. The latter contains a grid and is of wide area and low pressure, the object being to obtain a relatively slow passage of the gases through the furnace. The size of the slots in this grid is important, and  $\frac{7}{16}$  in. width has been found desirable. When the recuperated combustion air has reached a temperature approaching

200° C., powdered anthracite is gradually substituted for bituminous coal by the operation of a simple valve. Two pulverisers of the ball mill type are used, and the following specification has been laid down for the powdered fuels :

*Bituminous Coal* :—85% minimum to pass through a British Standard 200-mesh sieve.

*Anthracite Coal* :—99.3% minimum to pass through a British Standard 120-mesh sieve.

This might be compared with Kittredge's <sup>(5)</sup> specification when making steel for castings in the basic open-hearth furnace. Using Pennsylvania coal with 58% of fixed carbon and 4.5–7.9% of ash he requires that a minimum of 90% shall pass through a 240-mesh screen. The cost of pulverising and delivering this coal to the furnace is given as \$2.03 per ton, and 474 lb. of coal are used per (short) ton of metallic charge.

Anthracite contains about 10% of volatile matter with about 0.8% of sulphur, and has a higher calorific power than bituminous coal. By its use it is claimed that (a) there is less likelihood of contamination of the charge by ash and sulphur, (b) the lower content of hydrocarbons gives a low concentration of steam in the combustion chamber, which means reduced oxidation of the charge, and (c) the short flame of anthracite gives a more localised heating. On the other hand, the anthracite flame is less luminous than that of bituminous coal, and the authors have considered increasing its luminosity and therefore the radiated heat either by admitting a certain admixture of bituminous material or, alternatively, by injecting oil or lampblack into the burner. The sulphur pick-up during steelmaking amounts to 0.02% maximum.

For this type of furnace it is claimed that heat radiated from the flame to the charge is reinforced by actual conduction from the hot roof as it passes beneath the slag and bath during rotation. Furthermore, difficulties due to hard taps are avoided, whilst a portion of the metal charge may be removed at any time without emptying the furnace. The whole of the slag cannot be poured off without completely emptying the barrel, but a portion may be removed from the end port.

#### (4) Operation.

The charge is introduced horizontally into the furnace from boxes by a standard type of ground charging machine. Up to 13.5 cwt. of turnings may be charged. In some heats a small amount of anthracite is added with the steel scrap, which, together with a little pig iron, provides carbon to induce a boil. After very many early trials it has been found that to produce a boil and work down the charge in a more or less orthodox way is simpler and produces better steel than to attempt a direct fusion process without boiling. Perhaps the early heats became more oxidised than was



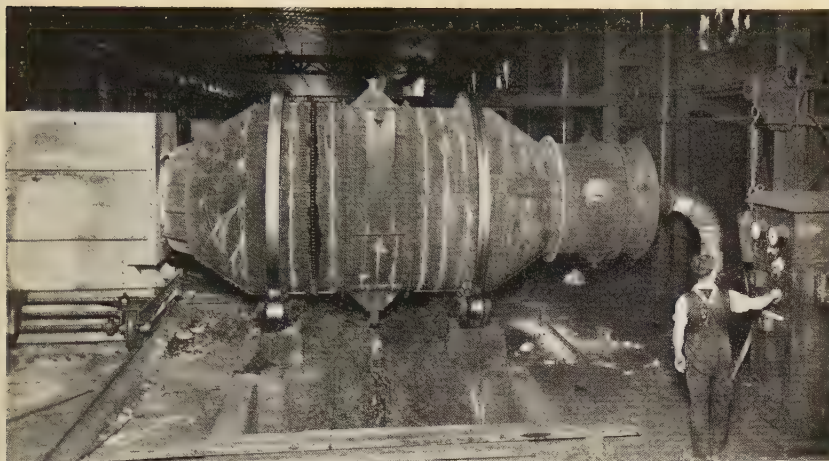
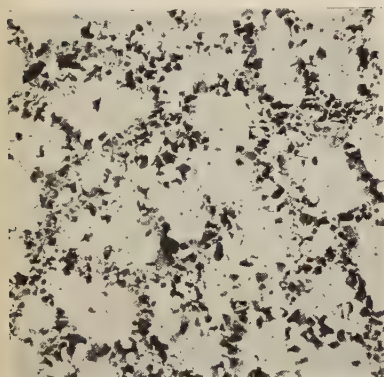


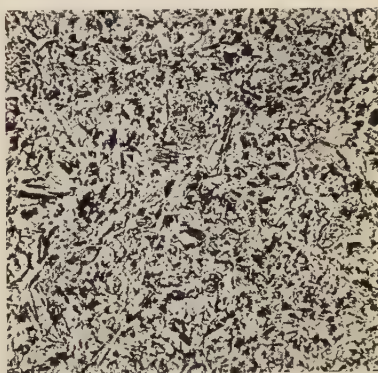
FIG. 1.—5-Ton Non-Reversing Sesci Furnace.



C. %.	Si. %.	Mn. %.
0.20	0.45	1.58
S. %.	P. %.	
0.050	0.046	

Yield point	25.0	} tons per sq.in.
Max. stress	35.4	
Elongation (2 in.)	29%	
Reduction of area	55%	
Izod value	42 ft.lb.	

FIG. 2.—Cast A/14/197. Fully annealed 900° C. Inherent grain size No. 7 A.S.T.M., fine.  $\times 120$ .



C. %.	Si. %.	Mn. %.
0.19	0.51	1.44
S. %.	P. %.	
0.050	0.044	

Yield point	25.5	} tons per sq. in.
Max. stress	39.5	
Elongation (2 in.)	25%	
Reduction of area	38%	
Izod value	20 ft.lb.	

FIG. 3.—Cast D/16/94. Annealed 880° C., then normalised 860–880° C. Inherent grain size No. 4–5 A.S.T.M.  $\times 120$ .

(Micrographs reduced to two-thirds linear in reproduction.)

[Lemon and O'Neill.  
[To face p. 56 p.]

C. %.	Si. %.	Mn. %.
0.19	0.51	1.44
S. %.	P. %.	
0.050	0.044	

Yield point . . . 24.6  
 Max. stress . . . 35.8  
 Elongation (2 in.) . . . 28%  
 Reduction of area . . . 51%  
 Izod value . . . 35 ft.lb.

FIG. 4.—Cast D/16/94.  
 Annealed, O.Q. 860–880° C., T. 650–670° C.  
 120.

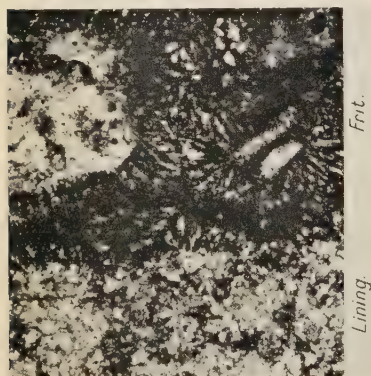


FIG. 5.—Junction of Frit Repair with Lining of Material A.  $\times 120$ .

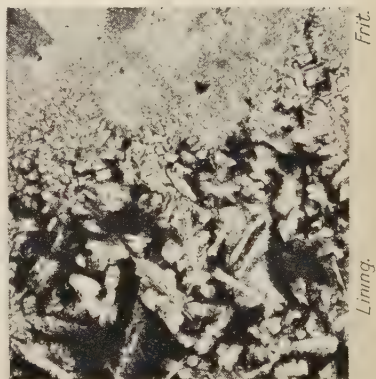


FIG. 6.—Junction of Frit Repair with Lining of Material B.  $\times 120$ .

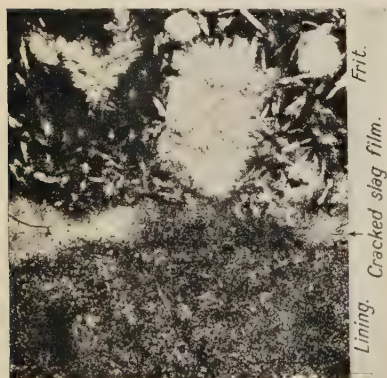


FIG. 7.—Junction of Frit Repair with Lining of Material D.  $\times 120$ .



FIG. 8.—Section of Patch Material after Fritting.  $\times 120$ .

Figs. 5 to 8. Ordinary transmitted light.  
 (Micrographs reduced to two-thirds linear in reproduction.)

TABLE I.—*Typical Heats.*

		Grade 1 Steel Heat A/14/192.		Grade 2 Steel Heat C/14/25.		
<i>Charge.</i>		Tons.	Cwt.	Tons.	Cwt.	
Locomotive tyres . . . . .			9		9	
Carriage tyres . . . . .			9		9	
Wagon tyres . . . . .			9		9	
Laminated springs . . . . .			9		9	
Laminated springs (Si-Mn) . . . . .			5		5	
Heavy mixed scrap . . . . .			18		9	
Gits and runners . . . . .			9		9	
Other scrap . . . . .			9	1	7	
Pig iron . . . . .			1		1	
Tyre turnings . . . . .			9	...		
Spiral springs . . . . .			9	...		
Total weight . . . . .		4	16	4	16	
Approx. carbon content . . . . .		0.45%		0.40%		
<i>Operation.</i>		Time.	Carbon. %.	Time.	Carbon. %.	
Furnace lit after charging . . . . .		4.20 P.M.		7.0 A.M.		
First sample . . . . .		6.25 "	0.15	9.0 "	0.15	
Boil commenced; 3 cwt. of pig and 120 lb. of limestone added . . . . .		6.27 "		9.5 "		
Second sample . . . . .		7.0 "	0.175	9.40 "	0.20	
Third sample . . . . .		7.30 "	0.15	10.25 "	0.16	
Fourth sample . . . . .		...		10.50 "	0.14	
Silico-manganese added . . . . .		7.36 "		10.55 "		
Ferro-silicon added . . . . .		7.39 "		...		
Ferro-manganese added . . . . .		7.42 "		10.58 "		
Tapped . . . . .		7.51 "		11.7 "		
Time of heat, charge to tap . . . . .		3 hr. 31 min.		4 hr. 7 min.		
Temp. of stream (uncorrected; disappearing-filament pyrometer)		1470° C.		1470° C.		
Composition.		O. %.	Si. %.	Mn. %.	S. %.	P. %.
Grade 1 heat : Before tapping . . . . .		0.15	...	...	0.051	0.040
Finished steel . . . . .		0.18	0.323	0.66	0.058	0.049
Grade 2 heat : Before tapping . . . . .		0.14	...	...	0.045	0.037
Finished steel . . . . .		0.19	0.542	1.56	0.046	0.040
Mechanical Tests of Annealed Cast Bars.	Yield Point. Tons per sq. in.	Tensile Strength. Tons per sq. in.	Elonga- tion on 2 in. %.	Reduction of Area. %.	Izod Value. Ft.lb.	Bend Test.
Grade 1 heat	19.8	30.4	35	55	...	180° U.*
Grade 2 heat	27.4	37.9	26	42	35	...

*Temperature.*

According to the corrections recommended by the Cambridge Instrument Co. for measuring the temperature of molten steel, a reading of 1470° C. would correspond with a true temperature of about 1600° C. By the courtesy of the British Cast Iron Research Association, temperature measurements were also made with their Bi-Optix instrument, and readings were of the order of 1550° C. The fact that during the repair of the lining the patch is partially fused shows that the temperature reaches 1600° C. approx. The effect of variations in emissivity upon observed optical pyrometer readings has been discussed by Todd (*Metal Treatment*, 1939, vol. 5, p. 171).

\* Unbroken.



TABLE II.—Working Data.

Ref. No.	Item.	Representative Sesci Furnace Data.	Example of Fixed Acid O.H. Furnace. <sup>(2)</sup>
1	Nominal capacity.	5 tons cast iron; 4 tons steel	35 tons
2	Tapping capacity.	First 4-5 heats, 4 tons; afterwards, 4½ tons of steel	43 tons
3	Average time from first to last tap of week.	54 hr.	126 hr.
4	Output of castings per week.	70 tons, including headers, &c.	341 tons
5	Output of castings per cast.	About 9600 lb. = 4.3 tons	38 tons
6	Time for making frit repair.	90 min. approx.	...
7	Output per hr. including fritting time.*	0.91 tons	2.4 tons
8	Contact reaction area of hearth per ton capacity.	67 4.3 = 15.5 sq. ft. approx.	6.65 sq. ft.
9	Output per sq. ft. of hearth area per hr.	30 lb.	19.0 lb.
10	Percentage of slag made.	425 lb. of slag per ton of finished casting = 19%	9.6%
11	Analysis of of slag :	With Lining Material.— †	
	SiO <sub>2</sub>	59.3%      62.2%	55.5%
	FeO	11.8%      12.5%	12.5%
	CaO	8.1%      9.44%	10.0%
	MnO	13.2%      12.6%	9.0%
12	Anthracite consumption per ton of castings.	2780 4.5 = 645 lb.	700 lb. (bituminous coal)
13	Therms (coal) per ton of castings (from gross calorific power of anthracite).	96	90-7
14	Average fuel analysis and calorific value.	Anthracite. Moisture 1.3% Comb. volatiles 10.9% Fixed carbon 81.0% Ash 6.8% 100.0% Sulphur 0.8% Cal. value 14,384 B.Th.U. per lb.	Producer gas. CO 20.4% OH <sub>4</sub> 3.2% H <sub>2</sub> 13.4%
15	Exit gas analysis and calorific value :		
	Carbon monoxide.	3.67%	
	Carbon dioxide.	15.85%	
	Hydrogen.	0.69%	
	Oxygen.	0.17%	
	Calorific value.	61 B.Th.U. per cu. ft.	
16	Air flow at full load at room temp.	1950 cu. ft. per min.	2180 cu. ft. per min.
17	Temp. of air entering burner.	420° C.	900° C. approx.
18	Charge :		
	Cold pig.	1.5%	46%
	Steel scrap.	98.5%	
19	Average analysis of charge :		Pig Analysis.
	Carbon.	0.45%	4.0%
	Silicon.	0.40%	2.1%
	Manganese.	0.69%	0.8%
	Sulphur.	0.040%	0.018%
	Phosphorus	0.045%	0.023%
20	Limestone per ton of castings.	C lining. 23 lb.      A lining. † 46.5 lb.	32.5 lb.
21	Iron oxide per ton of castings.	Nil	91 lb.
22	Fluorspar per ton of castings.	Nil	...
23	Other additions per ton of castings.	50% Fe-Si 3.2 lb. 80% Fe-Mn 6.3 lb. 17/72 Si-Mn 24.4 lb. 54/32 Alsimin 0.46 lb. } to ladle 32/60 Ca-Si 1.4 lb. } Aluminium 2.0 lb. to moulds	

\* That is,  $\frac{(\text{Tons per week}) - (\text{Tonnage of first cast})}{(\text{Time from first to last tap})}$ .

† See Table VII.



TABLE II.—(continued).

Ref. No.	Item.	Representative Sesci Furnace Data.	Example of Fixed Acid O.H. Furnace. <sup>(6)</sup>
24	Bath dimensions (4.3 tons of metal): Length. Breadth.	12 ft. overall 3 ft. 10 in.	28.0 ft. 11.5 ft.
25	Contact reaction area per ton capacity.	15.5 sq. ft.	6.65 sq. ft.
26	Mean bath depth.	10.5 in. (max. 17 in. approx.)	9.25 in.
27	Dimensions of recuperators: Cross-sectional area of: Air uptake. Burner downtake.	0.55 sq. ft. 1.3 sq. ft.	8.0 sq. ft. ...
28	Consumption of refractory per ton of castings.	365 lb.	128 lb.
29	Melting loss.	6½%	
30	Weight of original lining material: Barrel.	20 tons A pisé (dry), or 22 tons 13 cwt. C lining (wet)	
31	plus combustion chamber.	2 tons	
32	Total material for one daily frit.	9 cwt. 3 qr.	136 heats
	Life of lining.	120-130 heats	

desirable, but the interesting thing is that with acid-lined arc furnaces in the United States of America boiling-down is also considered necessary to obtain good castings.<sup>(6)</sup> In some few cases the authors have made additions of iron ore as an oxidant, but generally there appears to be enough oxidation during melting to promote the boil. Limestone additions are made to the slag after the first carbon sample has been taken.

If the furnace is starting cold a flow of bituminous coal is introduced into the air pipe, and the air temperature rises quickly to about 180° C. in 10-15 min. Gradually the bituminous coal is cut off, and only anthracite will be in use after 30 min. operation. The furnace is given a partial rotation every few minutes to assist in uniform heating, the intention being to melt down as quickly as possible in the hope of keeping the sulphur pick-up as low as possible.<sup>(7)</sup> Too much rotation at this stage causes the lining to suffer mechanical damage. After about an hour the charge becomes pasty, and the full rotational movement may be applied. A charge of  $4\frac{3}{4}$  tons of steel is clear-melted in about 2 hr., with considerable oxidation of carbon. Boiling soon takes place, and if ore is added carbon is removed at the rather low rate of about 0.002% per min. Samples of the metal are taken at intervals and tested by the Carbo-meter until the carbon has dropped to the required figure. Finishing additions are then made, and the metal can be poured after  $3\frac{1}{2}$ -4 hr. in the furnace. The tap-hole is opened and the ladle takes the steel away to the foundry. The furnaces are working two or three heats each day for 5-5½ days per week, and the details of typical heats given in Table I. afford an idea of the present practice.

At the end of each day the lining is examined and a patch is fritted on, if necessary, as described in Appendix A. Average

figures for performance are recorded in Table II.; the data for a 35-ton fixed furnace reported by the Open-Hearth Committee of the Iron and Steel Industrial Research Council <sup>(8)</sup> given alongside are the only ones available for rough comparison purposes.

### (5) *Quality of the Steel.*

Steelmaking in this plant commenced in 1935, and the procedure has been modified from time to time as experience has been gained. At the end of 1935, at the suggestion of Messrs. Thos. Firth and John Brown, Ltd., a 1-ton ingot was made of Sesci steel and examined by that firm. The ingot and slags were analysed (*see* Table III.) and reported upon by them as follows:

The only point worth remarking upon is the absence of  $\text{Fe}_2\text{O}_3$ . This is rather remarkable in view of the rather low temperature at which this furnace is operated. It is possible

TABLE III.—*Heat C12, September 12, 1935.*

Ingot.		Slags.					
			11.33 A.M.	12.00 noon.	12.45 P.M.	12.58 P.M.	Final from Ladle.
Carbon	0.17%	$\text{SiO}_2$ %	63.30	51.10	59.30	59.30	57.40
Silicon	0.35%	$\text{MnO}$ %	12.02	8.35	6.09	6.12	8.96
Manganese	0.81%	$\text{FeO}$ %	16.42	27.22	23.62	23.62	22.46
Sulphur	0.048%	$\text{Fe}_2\text{O}_3$ %	Nil	Nil	Nil	Nil	Nil
Phosphorus	0.042%	$\text{Al}_2\text{O}_3$ %	6.00	4.4	4.8	4.6	5.6
		$\text{CaO}$ %	1.60	7.00	4.60	4.80	4.40

that it is absent because of the reducing action of the coal, but it would need investigating to be sure. At the same time it has not much practical interest.

The ingot was sectioned longitudinally, one half being used for macro-examination and the other after forging for physical tests. The latter half was forged to 3 in. square, and

TABLE IV.—*Physical Tests on Forged Sample after Normalising.*

0.564 in.  $\times$  2-in. test-piece.

	Yield Point. Tons per sq. in.	Max. Stress. Tons per sq. in.	Elonga- tion on 2 in. %.	Reduction of Area. %.	Izod Value. Ft.lb.
Longitudinal .	22.0	33.2	35.5	61.0	100, 75, 66
Transverse .	20.0	33.5	30.0	46.4	30, 35, 42

the tests were taken from the top of the bottom third of the ingot. Table IV. shows the physical test results, which, if anything, are above the average.

V-segregates are well pronounced and there is some looseness in the centre, but that which is observed is entirely normal and has nothing to do with the method of manufacture. The cleanliness is considered to be above the average.

Finally, we should like to state that the results show that this process can make this class of steel equal to the best produced in other acid systems.

Analytical results from metal and slag samples taken in February, 1936, are given in Table V.

TABLE V.—*Heat A3/37.*

Time.	Metal.			Slag.			
	Carbon. %.	Silicon. %.	Manga- nese. %.	SiO <sub>2</sub> . %.	FeO. %.	MnO. %.	CaO. %.
11.25 A.M. Pig added to bring carbon to 0.3% for boil.							
11.50 „ Sample . .	0.26	0.110	0.06	65.7	18.1	3.6	8.4
12.5 P.M. „ . .	0.21	0.049	0.03	62.3	20.5	4.1	8.6
12.20 „ . .	0.19	0.045	0.03	63.3	18.7	4.1	8.4
12.53 „ After tapping .	0.22	0.243	0.69	62.3	19.4	4.6	8.7
Examples of tapping samples from a fixed acid furnace. <sup>(8)</sup>	0.16– 0.75	0.25	0.7– 0.85	55.5	12.5	9.0	10.0

The authors believe that most steels should be made under conditions of grain-size control. During March, 1936, studies were made of the inherent grain size of the Sesci steel, and from June of that year fine-grained steels have been produced in a general way by controlled aluminium additions. It is known<sup>(9,10)</sup> that aluminium in steel castings tends to give a sulphide-eutectic type of structure, existing as non-metallic membranes or chains round the crystal boundaries and leading to poor ductility values. On the other hand, Sims and Dahle<sup>(11)</sup> consider that if, instead of adding the usual  $\frac{1}{2}$ –1 lb. of aluminium per ton, the dose is increased to 3 lb. or more per ton, then the network formation is hindered, nodular inclusions predominate and ductility is restored. Many United States steel foundries using acid electric furnaces have confirmed this effect, but others did not find the extra aluminium to be advantageous.<sup>(12)</sup> Much depends upon the oxygen concentration of the steel when the finishing deoxidisers are added,<sup>(13,14)</sup> and this means that good slag control must be practised. It is also known that the addition of aluminium makes the steel flow more sluggishly,<sup>(15)</sup>

although aluminium up to 0.05% is said to increase the fluidity of red brass.<sup>(16)</sup> The authors' practice is to work the charge down to a standard condition, as judged in the ordinary way by slag samples, and to introduce some Alsimin (aluminium 54%, silicon 32%, iron 12%) into the ladle and aluminium wire into the runners of the moulds, the total aluminium addition being about 2 lb. per ton. The castings contain 0.010-0.020% of aluminium.

TABLE VI.—*Examples of Test Results and Specifications.*

Cast No. and Heat Treatment.	Yield Point. Tons per sq. in.	Tensile Strength. Tons per sq. in.	Elongation on 2 in. %.	Reduction of Area. %.	Izod Value. Ft. lb.	Inherent Grain Size (A.S.T.M.).	C. %.	Si. %.	Mn. %.	S. %.	P. %.
A14/197	25.0	35.4	29	55	42	Fine, No. 7	0.20	0.45	1.58	0.050	0.046
B11/54	...	36.4	27	39	29	Fine, No. 6	0.20	0.505	1.31	0.045	0.046
B15/29	26.2	37.2	28.5	48	33	Fine, No. 7	0.20	0.505	1.51	0.051	0.046
A14/93	25.8	39.2	25	43	28	Fine, No. 6-7	0.20	0.557	1.76	0.059	0.044
B/9/58	...	29.2	31.5	46	33	Fine, No. 6	0.17	0.14	0.39	0.048	0.044
Cast C14/114. Annealed 900° C., furnace-cooled 4-5 hr. . . . .	26.4	37.7	27.5	50	31	Coarse, No. 4	0.19	0.56	1.60	0.054	0.047
Annealed 900° C., A.C. . . . .	26.6	38.2	19.5	28	27	...	...	...	...	...	...
O.Q. 870° C., T. 660° C. . . . .	22.4	38.0	23.0	35	23	...	...	...	...	...	...
Specifications. J. O. Arnold's re- commendation (anneal and nor- malise) . . . . .	...	30	20	...	...	...	0.35	0.3	1.0	0.07 max.	0.07 max.
Goodyear tyre moulds (normal- ise) . . . . .	16	31	15- 20	...	...	...	0.22- 0.28	0.45- 0.5	0.75- 0.85	0.09- 0.12	0.03- 0.05
B.S.S. 24-1930. (a) General railway	...	26 min.	20 min.	...	...	...	...	...	...	0.060 max.	0.060 max.
(b) For wearing surfaces . . . . .	...	35- 40	15- 10	...	...	...	...	...	...	0.060 max.	0.060 max.
U.S.A. wheel centres (Q. and T.) <sup>(13)</sup> . . . . .	24	38	22	...	...	...	0.28- 0.35	0.35- 0.45	0.85- 0.90	About 0.04	About 0.04

Table VI. gives some typical results together with certain specifications, the chief point of interest about the latter being the amount of sulphur and phosphorus which may be tolerated. The authors doubt whether 0.07% of sulphur is harmful for the details required at Crewe, but the warning of McCance<sup>(7)</sup> that "in intricate castings the danger of hot tears is substantially reduced if the sulphur is kept below 0.020%" must be borne in mind. Phillips<sup>(17)</sup> has



reported that tearing is associated with the presence of elongated colonies of inclusions, and that a sufficiency of aluminium causes small globules of  $\text{Al}_2\text{S}_3$  to form and cracking is reduced. Hot tears have not caused any pronounced trouble with the present steel, but non-metallic inclusions in a boundary-network formation certainly provide the main difficulties in the way of good ductility and bend test values. The present aim is to produce castings containing manganese 1.0–1.5%, silicon 0.3–0.5% and aluminium 0.02%; a typical microstructure after full annealing is shown in Fig. 2. The cellular arrangement of the pearlite shown is presumably due to the slow furnace-cooling permitting too long a time between the upper and lower change points, and a normalised structure such as that in Fig. 3 is probably to be preferred. Ageing of test bars for eight weeks produces no changes in mechanical properties.

Quenching and tempering treatments are not usually applied, but it may be of interest to mention that one American railway company is reported<sup>(18)</sup> to have ordered heat-treated carbon instead of annealed alloy steel wheel centres. Some particulars of this proposal are given at the bottom of Table VI., and the structure of one of the present authors' castings after quenching and tempering is shown in Fig. 4.

#### (6) *Lining Material.*

Most linings in use with rotary furnaces are of the monolithic type, consisting of graded quartz bonded with 15–35% of clay material and 6–7% of moisture to give a rammable mixture. This clay content generally corresponds with 5–10% of alumina, and other oxides are present to about 1%. Alternatively specially moulded silica bricks have been used, and British Patent 432,213, by W. Scott, covers an outer lining of refractory ganister or cement and an inner lining of refractory brick. Spalling troubles with the brick present difficulties and they have not been used in the furnaces at Crewe. The monolithic refractory is spread out and watered, after which tempering is allowed to proceed for some weeks. The furnace barrels are stood on end and fitted inside with a built-up template which may be taken apart in sections. After tempering, the lining is applied by working from the bottom upwards and ramming with chisel-edged pneumatic tools. Ramming with the barrel in a horizontal position has not given good results. The barrels are allowed to dry on end for about a month with a daily coke fire underneath, except at week-ends, after which they are mounted on their rollers. A timber fire is then maintained inside the barrel for at least  $3\frac{1}{2}$  hr., followed by coal firing until the air preheat temperature reaches  $350^\circ\text{C}$ ., and concluding with a slag glaze continuing until the preheated air temperature is at  $400^\circ\text{C}$ . Pig melts have not been employed, and the new lining goes straight on to steel manufacture. Experience has proved that when once

a lining has been brought into a good working condition, it pays to use it intensively and to shut down as little as possible. Continuous working would probably be economical, but so far only two shifts per day have been run, and the furnace has been kept warm overnight and at the week-ends.

The economical success of the process as a whole depends chiefly on the durability of the lining. The refractoriness of the latter is only one of several factors involved and the particle size grading of the mixture is of equal importance. Changes of density take place during the firing of a new lining, owing to the conversion in

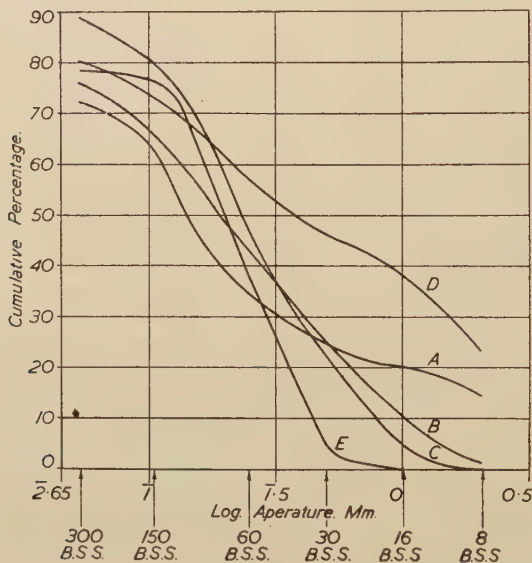


FIG. 9.—Grading of Sesci Furnace Lining Materials.

the quartz caused by heat, and Dawson<sup>(19)</sup> considers that the ramming density should be 2.2 to 2.3 to accommodate the quartz expansion at 573° C. Tests made on one of the authors' linings show that the density when rammed is about 2.1.

Monolithic lining materials from ten different firms have been tested and about five different mixtures have actually been installed in the furnaces. A French pisé was first employed and gave reasonably good life, but British material is now in use. As the lining becomes damaged during service it is economical to try and patch those areas which have worn most, and this has led to the utilisation of a patching or fritting technique described in Appendix A. Curiously enough, only certain types of lining material seem to be able to hold these fritted patches, and a mixture which is satis-

factory from the point of view of refractoriness and expansion may give only a low overall life in the furnace because of the difficulty of applying frits to restore its surface.

A detached specimen of the authors' frit material after use in the furnace gave the following results on a refractoriness test :

Initial deformation of test-piece. Cone, 26-27. Temp., 1580-1610° C.  
Squatted. Cone, 29. Temp., 1650° C.

The properties of some unfired linings are given in Table VII. and their particle grading is plotted in Fig. 9. Materials *A* and *B* are satisfactory both in performance and for taking fritting repairs; *C* and *D* are much less satisfactory, and *E* has not yet been tried in practice. Lining *F* collapsed during heating-up, and this indicates the importance of particle size in relation to performance.

TABLE VII.—*Properties of Lining Materials (dried at 100° C.).*

Material :	A.	B.	C.	D.	E.	F.
Ultimate Analysis.						
Silica. % . . . . .	90.13	87.3	87.6	72.4	83.4	90.9
Alumina. % . . . . .	5.36	8.2	7.6	18.7	10.6	4.9
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> ). % . . . . .	0.95	...	...	...	0.7	0.9
Loss on ignition. % . . . . .	1.56	3.0	2.7	2.6	3.1	2.3
Total . . . . .	98.00	98.5	97.9	93.7	97.8	99.0
Rational Analysis (approx.)						
Quartz. % . . . . .	79.3	77.0	78.4	52.3	...	...
Calcined china clay. % . . . . .	...	...	...	28.2	...	...
Clay. % . . . . .	17.7	21.6	19.4	19.5	...	...
Total . . . . .	97.0	98.6	97.8	100.0	...	...
Properties of Rammed Test-Pieces, fired at 1350° C.						
Apparent porosity. % . . . . .	24.5	31.0	35.3	33.0	34.3	24.9
Fired density . . . . .	1.85	1.76	1.66	1.73	1.68	1.90
Linear expansion. % . . . . .	+1.0	...	...	...	+1.1	+1.3
Properties of Rammed Test-Pieces, fired at 1600° C.						
Linear expansion. % . . . . .	} Incipient fusion	+1.3	...	+1.61	-0.1	...
Appearance . . . . .		Glazed	...	Glazed	Glazed	...
Particle Grading.						
On 8-mesh . . . . .	15	2	0	23	0	0
Through 8, on 16-mesh . . . . .	5	9	4	15	0	1
" 16, " 30 " . . . . .	4	15	18	8	4	1
" 30, " 60 " . . . . .	10	21	27	12	41	7
" 60, " 150 " . . . . .	29	19	30	14	31	34
" 150, " 300 " . . . . .	9	9	9	8	2	21
" 300 " . . . . .	28	25	12	20	22	36

Linings *A* and *F* have similar ultimate analyses, but their grading shows a marked difference. The bad lining *F* consisted of silica sand of fairly uniform size (through 60 and on 300 mesh), lacking coarse particles, and bonded with refractory clay. Good lining *A*, on the other hand, was composed of a mixture of *prefired* siliceous material for its coarsest fractions, with silica sand in the finer fractions, and a similar clay bond.

Further details concerning the properties of refractory monolithic linings are given in Appendix *B*,

*Acknowledgments.*

Acknowledgment is made to colleagues in the Chief Mechanical Engineer's Department and the Research Department who have assisted in the work, and to Sir Harold Hartley, F.R.S., Vice-President of the London, Midland and Scottish Railway Company, for permission to publish the results.

*APPENDIX A.—A Patching Process for Sesci Furnace Linings.*

By T. FLETCHER (LONDON, MIDLAND AND SCOTTISH RAILWAY COMPANY, CREWE).

The technique of fritting or fettling the Sesci furnaces at Crewe has needed considerable care and patience over a number of years. From a very humble beginning of 29 heats to our present record of 226 heats per lining is a very good step forward. At the beginning those who installed the furnaces taught us to repair the lining each night with the same French pisé as was used for ramming the barrel. This method was continued for a considerable time without giving very good results. The repair was usually lost during the working next day. In addition we found considerable difficulty in sampling the molten steel, owing to the working slag with partly dissolved lining being very hard and difficult to penetrate with the sampling spoon.

At an early stage it was decided to experiment with a mixture of 25% of Belgian silica sand and 75% of used pisé (or new pisé to make up), together with some residual slag, whereupon it was found that the repair stood up much better to work during the following day. We developed along these lines until eventually the patching mixture had become 75% of silica sand and 25% of used pisé, introduced by means of a furnace charging box with a movement of the charging arm through about 20° when applying the material. Full heat was then applied and partial fusion resulted. It was possible by this time to maintain each applied frit until the whole lining had been repaired in sections. We do not attempt to make a complete concentric ring; we are quite content to cover a sixth part of the lining, and the following day we usually put a patch on the opposite side. This is done to keep the barrel fairly evenly weighted and to avoid undue strain on the driving chain. This process is continued until at the end of a week the whole barrel is covered with this mixture.

The slags are much better with this method than with the original one, and we rarely have trouble unless one of the frits is lost. In this case the addition of limestone usually gives us a reasonably fluid slag, though it may perhaps prolong the time taken to obtain the heat.

Prior to the outbreak of the war we had a plentiful supply of Belgian silica sand. This was, and is still, in the author's opinion, the best that we have tried. Since the war, however, we have had



to use other sands of English origin. The best we have found and which we are now using is Chelford sand. We use this in the same amount as the Belgian sand, and regularly obtain 125 heats per barrel from the mixture. The following are particulars of the silica sands employed :

	Belgian Silica Sand	Chelford Sand.
Moisture. % . . . . .	0.13	6.3
Sample dried at 105° C.:		
Loss on ignition. % . . . . .	Nil	0.5
Silica. % . . . . .	99.88	93.8
Clay. % . . . . .	0.22	1.76
Fineness Tests :		
On 16 B.S. sieve . . . . .	Nil	0.1
" 30 " " . . . . .	0.4	2.0
" 60 " " . . . . .	43.2	32.3
" 150 " " . . . . .	55.8	58.1
Through 150 B.S. sieve . . . . .	0.6	7.5
	100.0	100.0

As the original pisé was a Continental product, a British lining material was sought for and is now used instead for the repair. After each day's work a frit made up of Chelford sand and either new or old lining material with a small addition of slag is put into the furnace and full heat is applied.

#### APPENDIX B.—*Tests on Refractory Lining Materials.*

By J. N. BRADLEY, A.R.S.M., B.Sc. (LONDON, MIDLAND AND SCOTTISH RAILWAY COMPANY, DERBY).

Simultaneously with the development of a working technique for the Sesci steel plant, laboratory tests were made on lining materials. In the early stages, linings of Continental origin (materials *B* and *C*, Table VII.) showed superiority over British materials, and this superiority persisted until the frit method of patching had been evolved. Thus, the refractories problem must be considered from two points of view :

- (a) The physical properties of the actual lining material.
- (b) The ability of the lining to unite with and hold a frit as its working face.

The early superiority of Continental linings was at first thought to be due to a more refractory composition and a small after-expansion or -contraction on firing.

After developing in the laboratory a lining made from British ingredients which was equal or superior in refractoriness and volume stability to those hitherto employed in practice, service trials showed that the ability to hold a frit was by far the most important factor, and the one upon which successful economic working of the Sesci plant largely depended.

*The Testing and Development of Monolithic Refractories.*

In the course of a systematic examination of lining materials submitted for trial the following tests were usually made:

- (a) Chemical analysis.
- (b) Grading.
- (c) After-expansion or -contraction at 1350° and 1600° C.
- (d) Physical properties of test-pieces rammed and subsequently fired at 1350° C.

In a few cases where the material was complex the separate mineral components were isolated and a complete view of the composition was obtained. It was found that two of the Continental manufacturers had introduced calcined china clay to minimise the permanent expansion of the quartz on firing, and one of these performed well in service.

Dependence on foreign supplies led to the utilisation of British sources. Both clay- and lime-bonded quartz were tried, but, although a lime bond is known to be giving good results in some foreign rotary furnaces, in our experiments the material proved to be very friable.

Eventually a satisfactory mixture as regards refractoriness and volume stability was produced, and later a segment was rammed in one of the Sesci barrels and tried out in service. Its composition and grading were as follows:

- (a) 54 parts of Welsh quartzite graded to :
 

Through 8, on 25 B.S. sieve . . .	76-80%
" 25, " 72 " " . . .	15-13%
" 72, " 150 " " . . .	} 9% max.
" 150 B.S. sieve . . .	
- (b) 31 parts of calcined china clay graded to :
 

Through 8, on 25 B.S. sieve . . .	10-13%
" 25, " 72 " " . . .	10-13%
" 72, " 150 " " . . .	32-26%
" 150 B.S. sieve . . .	Balance
- (c) 15 parts of high-grade fireclay pulverised so that 80% passed through a 150-mesh B.S. sieve.
- (d) 0.5% of sulphite lye.

The after-expansion when fired at 1600° C. was +1.5%, and the resistance to slag penetration was good.

Service trials were disappointing, as, whilst the refractoriness and volume stability were adequate, the necessary fritting technique then in operation did not permit of successful repair, and the lining soon wore away.

At this stage synthetic British linings were again tried in service. One particular proprietary mixture (material A, Table VII.), consisting of clay-bonded silica, in which the high permanent expansion of the quartz had been minimised by the incorporation of prefired siliceous material, behaved well in service, and has now come into regular use.

*Examination for Patching Ability.*

The patching process evolved at Crewe Works is described in Appendix A. Essentially this method enables a very high-silica frit to be used as the working face of the furnace, and by a careful and systematic procedure the frit-refractory junction is removed from the zone of reaction. This technique bears some resemblance in principle to the Clarkdale hot-patching of furnaces.<sup>(20)</sup>

It is an interesting problem as to why some lining materials are not easily patched in this way. Specific gravity determinations on specimens taken from old Sesci linings showed that at a depth of one inch behind the working face the temperature had not exceeded 1350–1400° C. This indicated that the refractoriness of the material was not of first importance when the above method of patching was used—a view borne out by the behaviour of various linings in service trials. It also suggested that the thermal insulation of Sesci furnaces would be undesirable while the frit repair method is in use. What did appear to be of great importance, however, was the nature of the bond between the frit layer and the refractory itself, as upon this depended the adhesion of the former when subjected to the rough usage which occurs in a rotary furnace.

Petrological and physical examination of a number of specimens taken from old linings which have successfully carried patches suggests the generalisation that materials which have formed a fairly strong ceramic bond at the working temperature of the furnace, and which have a low apparent porosity, do best in service. Figs. 5, 6 and 7 show the junction in three different linings, the first two of which were satisfactory and the other poor in service. In the poor material a cracked layer of slag separates the frit from the refractory. In the good materials no slag film is present and there is penetration and bonding of the matrix across the junction. The structure of the fired frit can be seen in Fig. 8; it consists of grains and needles of cristobalite.

It is well known that quartz undergoes a sudden and reversible expansion at about 575° C. This necessitates great care being taken during the initial firing of the lining and on all subsequent occasions when the lining has dropped below this temperature, as may sometimes occur at week-end stoppages. Patching frits are much more liable to be lost on starting up after such occasions than at any other time. This points to the zone of weakness being at the frit-refractory junction.

A tenacious slag layer which is not absorbed owing to the nature of the base refractory may explain the non-adherence of some frits. Differences in coefficients of expansion probably cause cracks in the interfacial layer, and failure follows. Satisfactory adherence of the frit is favoured by a low apparent porosity and good mechanical strength in the base refractory. No separating slag film should form or be present, and recrystallisation of the quartz to form

interlocking crystals at the junction of the two is desirable. The section of frit illustrated in Fig. 8 had the following chemical analysis :

Silica	.	.	.	.	.	.	78.3%
Alumina	.	.	.	.	.	.	2.6%
Iron (calculated to ferrous oxide)	.	.	.	.	.	.	8.6%
Manganese (as manganous oxide)	.	.	.	.	.	.	4.2%
Lime	.	.	.	.	.	.	2.6%
Total	.	.	.	.	.	.	96.3%

In general it has been found that the FeO figure should not exceed 5%. This shows that approaching 30% of steelmaking slag was present in this frit, but such a figure may not be truly representative. Thus, the slag content of the frit shown in Fig. 6, which did very well in service, is certainly lower. Measurements of refractive index show the frit in Fig. 8 to consist of partially dissolved pieces of quartzite, converted to cristobalite, with cristobalite dendrites in a complex silicate glass. The latter has a refractive index of 1.52.

The testing of new supplies of lining has now been altered so that less importance is attached to refractoriness, provided that this is adequate. Test-pieces are rammed to the same degree as that prevailing in the Sesci barrels themselves, and, after firing at 1350° C., apparent-porosity and compression-strength measurements are made. The permanent after-expansion of the lining is carefully watched, because if this is unduly large furnace shell bolts may be broken and cause the collapse of the structure.

The essential characteristics required in refractories employed in this way are still not clearly understood, but as further service data are obtained it is hoped to confirm the view put forward above.

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### CORRESPONDENCE.

Mr. C. H. WILLIAMS (Messrs. Stein and Atkinson, Ltd.) wrote : I have been much impressed by the extensive research that has been carried out by the authors in connection with the refractory linings. The success obtained with the fritting system overcomes what has always been the main handicap in using rotary furnaces for steel castings, and the results cited by the authors for lining performances certainly speak for themselves.

I notice that the time taken for making a frit repair is given as 90 min., so presumably the furnace has to be fired for something over 1 hr. after the patching mixture has been charged into position ; I should like to know if this assumption is correct. Also, is it satisfactory to apply the patch on top of the normal small quantity of slag which remains in the bottom of the furnace after the ordinary slag emptying or is it necessary to take any special precautions to ensure an absolutely clean surface for the patch to rest on ? When using old lining material in the patching mixture is the presence of small lumps detrimental and is it advisable to put the material through a grinding mill ?

Another aspect on which I would appreciate the authors' comment concerns the degree of incorporation of the finishing additions in the bath. I have personally encountered occasions when it has been difficult to make certain that all the additions get down through the slag and sometimes have found it helpful to lighten

this by adding fluorspar. Most foundries in my experience regard drawing off slag through the exhaust opening as too arduous and tedious a job to be carried out regularly and as a result the tendency sometimes is to use an excess of final additions to compensate for the quantity held up in the slag. I should be interested if the authors could state the actual percentages of the silicon, carbon and manganese contents of the additions to the bath which they find in practice are incorporated in the molten metal.

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### *AUTHORS' REPLY.*

The AUTHORS wrote in reply to Mr. Williams : The furnace is fired for just over an hour after the patching mixture has been applied at the end of the day. No special precautions are taken to obtain an absolutely clean surface before the frit material is charged, and actually a small amount of slag always remains on the lining. The presence of small lumps in the old lining patching material is not considered detrimental, and a grinding mill is not employed.

Slag is not drawn off through the exhaust opening, and it is also rather tedious to pour it off through the tap-hole and make good the latter afterwards. Difficulty has sometimes been experienced in getting all the alloy additions through the slag, but rabbling is carried out and found to be effective. For a Grade 2 heat about 0.07% of carbon, 0.40% of silicon and 2.20% of manganese are added to the bath in the form of finishing alloys. From the analysis of the finished steel in heat C/14/25 (Table I.) it will be observed that there is about a 30% loss of manganese.

# A STUDY OF SOME SOLUBLE INHIBITORS, WITH SPECIAL REFERENCE TO HEAT TRANSFER AND WATER-LINE ATTACK.<sup>1</sup>

• BY R. S. THORNHILL, PH.D.,

WITH AN EXPLANATORY STATEMENT BY U. R. EVANS, SC.D.,  
(CAMBRIDGE UNIVERSITY).

*Paper No. 7/1942 of the Corrosion Committee.*

(Fig. 3 = Plate V.)

## SYNOPSIS.

Experiments have been carried out to ascertain whether magnesium chromate belongs to the "safe" or the "dangerous" class of inhibitors. Tests upon steel partly immersed in various natural waters under conditions of alternate heating and cooling indicate that, if rusting is to be avoided, magnesium chromate must be replenished at certain intervals. But even if the periods elapsing between replenishments are double those needed to avoid all corrosion, the steel suffers little thinning over periods sufficient to cause perforation of steel in similar water without chromate. In cases where steel was allowed to start rusting before the inhibitor was added, the rusting ceased after the addition of the inhibitor. On the other hand, experiments without heating under stagnant conditions showed that steel carrying mill-scale interrupted by a scratch-line suffered more rapid thinning when inadequate amounts of the inhibitor were added than in similar water without inhibitor. Both potassium chromate and basic magnesium chromate decrease the total corrosion as the amount added is increased, but the intensity of attack, owing to localisation, is at first greatly increased. Thus, both of the inhibitors belong to the dangerous class.

The intense localised corrosion which occurs at concentrations intermediate between those permitting general corrosion and those conferring complete immunity sometimes takes the form of pitting. It may occur on any part of the specimen, but when the susceptible point is situated in or near the meniscus zone, the attack develops into a "box" of triangular cross-section, instead of the ordinary blister, and under these water-line conditions the attack is very vigorous. The fact that the water-line may sometimes be immune and sometimes specially attacked, according to the nature of the metal, the liquid and the time of exposure, is capable of a consistent explanation. Another cause of water-line attack has been found in the condensation of moisture, free from inhibitor, above the water-line; where this trickles down, it produces an area locally weaker in inhibitor, giving rise to the cell:

Iron | Concentrated inhibitor | Diluted inhibitor | Iron.

<sup>1</sup> Received August 25, 1942. This paper is published by authority of the Corrosion Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

Measurements of heat transfer through steel walls show that under conditions where the corrosion product would cling to the walls and obstruct heat transfer, the presence of basic magnesium chromate improves the situation by preventing the formation of that corrosion product. However, in the waters studied, the corrosion product does not cling to the walls under conditions of alternate heating and cooling, so that in effect the presence of the inhibitor has little influence on heat transfer.

## PART I.—EXPLANATORY STATEMENT AND RÉSUMÉ OF CONCLUSIONS.

By U. R. EVANS, Sc.D.

*General.*—This explanatory statement serves to indicate the problems which Dr. Thornhill's research was designed to solve, and to summarise the conclusions which may be drawn from his work. For a description of the experimental methods, the reader is referred to Dr. Thornhill's part of the paper.

*The Functions of a Soluble Inhibitor.*—Soluble inhibitors of corrosion are mainly used as additions to waters circulating through steel heat-exchange systems, and particularly cooling systems. Although a typical system of cooling pipes or cooling jackets may in theory be kept completely full, air spaces or adherent air bubbles are in practice apt to exist within them, and during periods of shut-down water-line attack may have to be considered. Spaces filled by air or nitrogen, however small, also affect the problem while the plant is in operation, since they will become hotter than the mass of the metal, giving rise to the hot-wall effect discussed by Benedicks.<sup>1</sup> At the edge of gas spaces the direction of flow of heat is more nearly parallel to the metal surface than at right angles to it, and this must be borne in mind when devising laboratory experiments to explore the situation; the use of a specimen immersed in liquid thermostated at the required temperature does not represent these particular conditions.

The inhibitor may fulfil two purposes :

- (1) To diminish the total amount of corrosion, thus diminishing the volume of rust sludge which might otherwise obstruct water flow, and possibly interfere with heat transfer.
- (2) To diminish the rate of thinning of the walls, thus avoiding premature perforation or breakage.

Now, clearly any inhibitor will to some extent fulfil the first purpose, for a chemical which failed to reduce the total corrosion could not be called an inhibitor. But many inhibitors will under certain conditions fail to reduce the rate of thinning; on the contrary,

<sup>1</sup> C. Benedicks, *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1925, vol. 71, p. 597; also *Ingeniörs Veterkaps-akademien*, 1927, Handlingar Nr. 60.



they may often increase it if the attack, although diminished in total amount, is concentrated on a small fraction of the metal, so that the intensity of attack may be locally greater than if no inhibitor had been added. This localised attack frequently occurs at a water-line or at the boundary of an air space. The intense attack produced along the water-line at unfortunate concentrations of inhibitor has been studied by the author in early papers.<sup>1</sup> It also occurs where inert material rests against the metal surface, producing a crevice where the inhibitor may become exhausted more readily than elsewhere. The tendency of intense corrosion to set in at crevices, cracks and re-entrant corners, as well as at places where débris, loose mill-scale or tubercles of old rust have lodged, is often met with in service. It has, for instance, been discussed by van Brunt and Remscheid<sup>2</sup> in connection with the cooling jackets of power rectifiers fed with water in which sodium dichromate was used as inhibitor.

Electrochemical considerations have led the author<sup>3</sup> to the conclusion that, in cases where the corrosion process is controlled by the *cathodic* reaction, the addition of any inhibitor which acts by restraining the *anodic* reaction, in quantity insufficient to protect the whole surface, is likely to *increase*, instead of reducing, the *intensity* of corrosion. Such an "anodic inhibitor" will restrict the area over which anodic attack takes place and increase the area available for the cathodic reaction. Since the control is cathodic, this will tend to increase the electric current passing, and, since the attack is concentrated on the now greatly diminished anodic area, the *intensity* of the attack (corrosion per unit area of the part affected) will be increased, notwithstanding that the *total attack* is diminished. In short, anodic inhibitors are liable to be dangerous. Cathodic inhibitors, on the other hand, are safe. Unfortunately, their action is often due to the deposition of a relatively thick film on the cathodic areas, and this may interfere with heat transfer; in any case, the reduction of the total corrosion by cathodic inhibitors<sup>4</sup> is never so complete as that produced by anodic inhibitors, which, if added in sufficient excess, may stop corrosion altogether. Thus, *anodic inhibitors are effective but dangerous*, whilst *cathodic inhibitors are relatively ineffective but safe*, for at least they will not make the intensity of attack worse than if no inhibitor had been added.

The effect of a dangerous inhibitor may become especially serious

<sup>1</sup> U. R. Evans, *Journal of the Society of Chemical Industry*, 1925, vol. 44, p. 165T; 1927, vol. 46, p. 347T. *Transactions of the Liverpool Engineering Society*, 1926, vol. 47, p. 218.

<sup>2</sup> C. van Brunt and E. J. Remscheid, *General Electric Review*, 1936, vol. 39, p. 128.

<sup>3</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1936, vol. 69, p. 213.

<sup>4</sup> C. W. Borgmann, *Industrial and Engineering Chemistry*, 1937, vol. 29, p. 816.

where the surface is covered with mill-scale interrupted locally, *e.g.*, by a crack or scratch-line. Even in the absence of inhibitor, such a surface might be expected to suffer intense localised corrosion, since the mill-scale provides a large cathode and the gap a small anode; as explained above, this combination of large cathode and small anode is always likely to lead to intense attack on the latter. However, in the absence of inhibitor, the corrosion tends to undermine the mill-scale, so that the attack, highly localised at first, becomes increasingly spread out with the passage of time. An unfortunate quantity of inhibitor, just insufficient to prevent attack altogether, will prevent this undermining process, and the corrosion, remaining highly localised, is exceedingly intense.

Another serious situation is where parts of the metal are covered with small patches of adherent rust. This rust may interfere with replenishment of inhibitor at the metallic surface covered by it, especially since any soluble iron salts in the rust will tend to precipitate the inhibitor. Thus, the rust-covered area remains anodic, and the rust-free portion, which the inhibitor can reach easily, will be the cathode. Here again we may obtain the combination of large cathode and small anode which so often produces intense localised attack.

It seemed highly important to classify soluble inhibitors according to whether they restrain the anodic or the cathodic reactions, and this has been done in the experiments of Chyżewski in the author's laboratory.<sup>1</sup> He found that sodium hydroxide and carbonate act both as anodic and cathodic inhibitors, zinc sulphate as a cathodic inhibitor only, and emulsifying oil as an anodic inhibitor. In the presence of alkali a chromate inhibits the cathodic reaction, but in the presence of acid there is marked stimulation at the cathode. Chromates act as anodic inhibitors in neutral, but not in acid, solutions.

It seemed possible that magnesium chromate might serve as an inhibitor which would be both safe and efficient. The chromate present would certainly restrain the anodic reaction, whilst the production of a film of magnesium hydroxide on the cathode might sufficiently reduce the total current to prevent intensification of the attack in case the dosage were too small to protect the whole of the surface. The author therefore suggested to Dr. Thornhill that he should carry out experiments to ascertain whether magnesium chromate was a safe or dangerous inhibitor. Since, however, there was a risk that the film of magnesium hydroxide might interfere with heat transfer, it seemed evident that a comparison of heat transfer in the presence and absence of this inhibitor was also necessary before it could be recommended in practice. This was also undertaken by Dr. Thornhill. Since the intense corrosion met with at unfortunate concentrations of inhibitors so often

<sup>1</sup> E. Chyżewski and U. R. Evans, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 215.

occurs at the water-line, Dr. Thornhill extended his work to ascertain the causes of water-line attack under these conditions. And, since it was felt that the attack might be modified and probably intensified where the heat entered the liquid from an unwetted part of the metal, special experiments were carried out in cells constructed to represent this mode of heat transfer; these latter experiments were largely performed by Mr. A. Shadbolt.

*Behaviour of Magnesium Chromate at Ordinary Temperatures under Stagnant Conditions.*—In order to represent the most dangerous state of affairs, specimens of steel were covered with oxide films by heating, and then a scratch-line was traced through the skin, exposing the bright metal. These were then partially immersed in liquids containing varying amounts of chromate; in some series of experiments potassium chromate was used and in others "basic magnesium chromate" (i.e., chromic acid with twice its equivalent of magnesia). The object of the excess of magnesia was to deal with any aggressive carbonic acid which might be present in the liquid. The liquids used were Cambridge tap water and also a chloride solution, since chromate-chloride mixtures, at an unfortunate ratio of the two salts, are known to give intense local attack. The number of specimens studied was 200 and the main experiments lasted 60 days. In order to measure the loss of thickness, Dr. Thornhill constructed an electrical apparatus for ascertaining the depth of pits or areas of local corrosion.

The results show that the total corrosion becomes less as the addition of inhibitor is increased. Unfortunately, they also show that basic magnesium chromate, like potassium chromate, is a dangerous inhibitor in the sense that small amounts, although reducing the total corrosion, greatly increase the loss of thickness of the steel at the parts most intensely attacked.

Thus, the main hope of the experiments—the discovery of an inhibitor which would be at once efficient and safe—has not been achieved. On the other hand, basic magnesium chromate may prove to have useful applications.

*Behaviour of Magnesium Chromate under Conditions of Alternate Heating and Cooling along the Metal.*—In the experiments performed by Mr. Shadbolt, the specimens partially immersed in water were used to transmit heat to the liquid; when a temperature of 50° C. was reached the liquid was allowed to cool down again. Some hundreds of these cycles were carried out in the course of each experiment. Here basic magnesium chromate was the inhibitor studied. The object was to ascertain whether water to which the inhibitor had been added in insufficient amount, or in which the replenishment occurred at intervals too infrequent to stop rusting altogether, would produce perforation more quickly or less quickly than similar water to which no inhibitor had been added at all. Here again some of the experiments were carried out on specimens which were already covered with oxide scale, interrupted locally at

scratch-lines. As expected, this tended to concentrate the attack, and perforation, when it arrived, occurred first at the scratch-lines at a time when the specimens which carried no mill-scale had not been penetrated. In other experiments, specimens were allowed to rust in water containing no inhibitor for four cycles before the inhibitor was added; the object was to ascertain whether the inhibitor would arrest rusting which had already started, and it was encouraging to find that this was the case. The inhibitor was clearly expended in the task of protecting the metal, and fresh amounts had to be added at intervals in order to maintain the protection. A special series was carried out in which the additions were made at intervals twice as long as those needed to prevent attack altogether. It was found that even this "stinted replenishment" rendered the thinning much slower than that which was produced in comparative experiments where no inhibitor at all was employed. These facts taken together seemed to suggest that under these conditions basic magnesium chromate was a "safe" inhibitor.

The encouraging results obtained under conditions of alternate heating and cooling seemed to contrast strangely with the discouraging results obtained under stagnant conditions at low temperatures. Actually, the initial dose of chromate used for the experiments with heating was sufficiently high to avoid local corrosion in the early stages. Probably the convection set up in the heating and cooling serves to avoid any very serious local exhaustion of inhibitor; moreover, the conditions were unfavourable to the formation of the triangular "box" at the water-line which, under stagnant conditions at low temperatures, preserves an area free from inhibitor and maintains the combination of small anode and large cathode—a combination so liable to lead to localised corrosion.

The experiments encourage the hope that in a plant in operation basic magnesium chromate might prove useful as an inhibitor, provided that the first dose added was fully adequate, and provided that care was taken that the concentration was brought well above the dangerous range before circulation was stopped and the conditions became stagnant. But further work would be needed before it could be applied in practice, and it may be better to use the experimental method developed to test other inhibitive mixtures which have suggested themselves as a result of the information gained.

*Measurements of Heat Transfer.*—If the prevention of corrosion by basic magnesium chromate depends even in part on the production of a cathodically formed film, it would be necessary to examine its effect on heat transfer before the inhibitor could be considered for use in practice. But the effect of inhibitors on heat transfer is important in another way, since it seems at least possible that the chalky scale which so often obstructs heat transfer may be really a corrosion product. A hard water containing calcium bicarbonate



will deposit calcium carbonate when heated, and, although this may often be produced as a sludge in the body of the liquid, it is always likely that, when the walls are hotter than the water, much of it will be deposited as an adherent scale on the walls. It is commonly believed by engineers that the chalky scale found on heated steel surfaces is formed entirely in this way, and if this belief is true the obvious remedy is to soften the water. On the other hand, it is not impossible that calcium carbonate may be thrown down as the cathodic corrosion product. Such a view has been held by Colbeck and others, but has never received widespread consideration from engineers, owing to the prevalent belief that the corrosion product of iron is iron oxide. Recent research has shown that, in corrosion by a water containing temporary hardness, calcium carbonate is thrown down on the cathodic portions and is only turned into rust through subsequent interaction with anodically formed iron salts. Thus, the scale may be either a rusty chalk or a chalky rust. The chalky deposit, if once started by corrosion, may subsequently provide nuclei for the thermally produced calcium carbonate, so that the thickness may increase. If it is true that the obstructive film originates from a corrosion reaction, then the addition of an inhibitor may be a more rational method of correcting the trouble than softening. Indeed, in extreme cases, softening by the base-exchange process may be actually unfavourable to heat transfer. Apart from the formation of sodium bicarbonate, such softening is apt to leave aggressive carbonic acid in the water, even if it was free from aggressive carbonic acid before softening; the reason for this has been explained elsewhere.<sup>1</sup>

To explore these possibilities, Dr. Thornhill carried out comparative measurements of heat transfer, using :

- (1) Cambridge raw water, which is essentially a solution of calcium bicarbonate;
- (2) the same water fully softened by base-exchange treatment, so as to convert the calcium bicarbonate to sodium bicarbonate;
- (3) the raw water rendered non-corrosive with basic magnesium chromate but not softened.

Eighteen hundred measurements of heat transfer were carried out altogether, but the results can be summarised briefly.

The first experiments concerned transfer through *vertical* metallic walls, and were carried out :

- (a) With a *deficiency of oxygen*, so that the rust was essentially *magnetite*,
- (b) with *excess of oxygen*, so that the rust was largely *hydrated ferric oxide*.

<sup>1</sup> U. R. Evans, "Journées de la Lutte contre la Corrosion," Group 3, No. VI., p. 492c. Paris, 1938.

Several heating and cooling cycles were carried out each day, but the apparatus remained stagnant during the week-end. It was found that during the week-end the heat transfer deteriorated in the case of the two waters free from inhibitor, evidently owing to the formation of corrosion products on the walls; in the case of the water containing inhibitor, there was no corrosion product and no deterioration of heat transfer. However, during the working week there was little alteration in the heat transfer, for the simple reason that when the water was in motion, owing to the heating and cooling, the corrosion product did not adhere to the walls but accumulated at the bottom of the apparatus. It was noticed in the case of the series conducted in a deficiency of oxygen that the amount of corrosion was greater, and the heat transfer worse, in the fully softened water than in the raw water (it should be made clear that this fully softened water is *not* the water supplied to the town of Cambridge).

It seemed possible that if the heat transfer was measured through the *horizontal bottom* of a vessel on which the corrosion product would accumulate, treatment with inhibitor would prove beneficial. Accordingly, a further set of experiments was carried out to test this point, but here also the addition of inhibitor produced no real improvement. It is believed that the heat, prevented from passing directly through the bottom owing to the accumulation of matter settling on it, moved laterally and passed up into the vertical walls, which were fairly free from corrosion product, thus reaching the water.

The conclusion is that, under the particular conditions studied, the improvement arising from the addition of inhibitor, although capable of being detected, was not important. It is satisfactory to note that no deterioration of heat transfer was caused by the protective film. The fact that under certain circumstances complete softening reduced the heat transfer is of some interest, but it should be added that other waters, particularly those containing calcium sulphate, might behave very differently. Time has not permitted a further study of this matter.

*Causes of Water-Line Attack.*—The fact that in the presence of an inhibitor intense corrosion often occurred on the water-line rendered it desirable to obtain more detailed knowledge of the mechanism of water-line corrosion. Accordingly, a detailed study of the distribution of corrosion in different waters containing different amounts of inhibitor was carried out, using not only magnesium or potassium chromates but also sodium carbonate and sodium vanadate, an inhibitor which, although with no commercial possibilities, is interesting in producing deep pitting when added in certain quantities. In all these cases localised corrosion, sometimes sufficiently intense to be styled pitting, occurred at concentrations intermediate between those which caused general corrosion and those sufficient to produce complete immunity. The intense

localised type of corrosion can be obtained even when no dissolved substance is present except the inhibitor; it occurs in sodium carbonate solutions in the absence of any other salt over a narrow range of dilute concentrations; but if chlorides are also present, it occurs at a higher concentration, where the attack is naturally faster, and extends over a wider range of concentrations. Thus, certain chloride-carbonate mixtures are in effect more dangerous than any liquid containing carbonate alone.

The intense localised corrosion which occurs when the inhibitor is present in an unfortunate concentration does not necessarily occur at the water-line, but if the susceptible point from which the localised corrosion develops is situated in or very near to the meniscus zone, the attack takes a particularly virulent course. The corrosion product which, in the presence of larger amounts of inhibitor, would be precipitated in physical contact with the metal, thus stifling further attack, tends to be precipitated on the curved surface of the water where it rises to meet the metal, and a "box" of triangular cross-section is formed, which shuts in a narrow strip of metal; the inhibitor soon becomes exhausted within the box, which becomes a small anodic area, whilst the large area outside the box, plentifully supplied with inhibitor, forms the cathode. This combination of large cathode and small anode leads to intense attack. The iron salts formed anodically within the box and the inhibitor present outside precipitate one another; this keeps in good repair the diaphragm constituting the lower side of the box, and prevents the entry of inhibitor into the box, where the iron remains anodic.

The reason why the triangular box formed at the water-line produces more damage than the blisters formed at susceptible points lower down may be partly due to the fact that a water-air interface constitutes a surface particularly favourable for the formation of the membranous type of hydroxide, but it may also be partly due to the fact that the ferric compounds formed in the presence of excess of oxygen are less soluble than the corresponding ferrous compounds. An important factor is that the intense local corrosion proceeding within the box requires a rapid supply of oxygen to the cathodic part of the metal immediately outside it, and this is best obtained at the water-line.

In general, the observations confirm the views on water-line attack previously held, but a different type of water-line attack in solutions containing inhibitor has been noticed by Dr. Thornhill.<sup>1</sup> Where condensation of moisture occurs above the water-line, this is naturally free from inhibitor, and, running down, will dilute locally the liquid at the water-line. The cell set up:

Iron | Concentrated inhibitor | Diluted inhibitor | Iron,

will have a large cathode and a small anode, leading to intense

<sup>1</sup> Since this was written, Dr. T. P. Hoar has informed the author of an industrial case of water-line attack apparently connected with condensation.

water-line attack. This form of water-line attack will only occur in confined spaces where the metal has become colder than the solution, but such a state of affairs is likely to arise in cooling systems containing an air-space shortly after the operation of the plant has been suspended.

It may be interesting to note that the explanations of water-line attack in the presence of inhibitor fit well into a theory of the distribution of corrosion lately published by the author.<sup>1</sup> It was shown therein that the expected intensity of corrosion at a point in an experiment lasting time  $T$  is :

$$uT - \frac{u}{p}(1 - e^{-pT}),$$

where  $p$  measures the probability of inception of attack, and  $u$  the conditional velocity (mass per unit time and area) with which it will subsequently develop. This expression approaches the limiting value of  $\frac{1}{2}upT^2$  for very short experiments and the limiting value of  $uT$  for very long experiments.

Now, on iron or zinc partly immersed in sodium chloride *in the absence of an inhibitor*,  $p$  will be minimal at the water-line, where oxygen, the cathodic stimulator, is easily replenished; for this part will tend to become cathodic, and sodium hydroxide, the cathodic product, is a powerful inhibitor. On the other hand,  $u$  will be maximal at the water-line, but will in general vary with level much less than  $p$ . For short experiments, where  $u$  and  $p$  enter symmetrically into the expression  $\frac{1}{2}upT^2$ , the expected intensity of corrosion will be least where  $p$  is lowest, thus explaining why, in the opening stages of corrosion, the water-line is free from attack. In the later stages, where  $p$  does not enter into the expression ( $uT$ ), the expected intensity of attack will be greatest at the water-line, since there  $u$  is highest. Thus, we arrive at the explanation of the apparently discordant facts that the *water-line is unattacked in the early stages and severely attacked in the later stages*.

*In the presence of sufficient inhibitor* to prevent corrosion over the greater part of the surface, the distribution of  $u$  and  $p$  will be changed. Since the total corrosion velocity, and hence the rate of oxygen uptake, is now small, the oxygen concentration at any point where corrosion is not already taking place will be much the same whether the point is near the water-line or far below it; moreover, where there is already a large quantity of inhibitor present, the production of sodium hydroxide, or other alkali, will have little effect on  $p$ . Thus,  $p$  will be sensibly independent of level. On the other hand, when once at a small point corrosion has set in, the local consumption of oxygen may be very rapid, and corrosion can only proceed readily if a good supply of oxygen is available. Thus,  $u$  will be maximal at the water-line, and will

<sup>1</sup> U. R. Evans, *Nature*, 1942, vol. 150, p. 151.



diminish rapidly as we pass away from it. Consequently, in the early stages of an experiment, where  $u$  and  $p$  enter symmetrically into the expression  $\frac{1}{2}upT^2$ , we will now find the expected corrosion to be greatest at the water-line, since  $u$  is maximal at that point, and  $p$  hardly alters with level. In other words, *in the presence of a quantity of inhibitor just insufficient to stop corrosion altogether*, attack may be expected to *set in at the water-line even in the early stages*; and this is found in general to be the case.

If this explanation is right, we may expect to find the water-line preferentially attacked even in the absence of inhibitors on those materials which form a highly protective oxide skin, but which corrode readily when once this skin has broken down. This is, indeed, found to be the case. On stainless steel, if corrosion occurs at all, it is frequently found at the water-line. Early studies of the corrosion of aluminium<sup>1</sup> showed that water-line attack was relatively important in the early stages. Hoar,<sup>2</sup> who has made a detailed study of the "black spot" corrosion of tin, has stated that this form of breakdown shows a rather special tendency to occur at the water-line.

Thus, speaking generally, the known facts seem to agree well with theory, but the situation is undeniably complicated, and doubtless other factors deserve consideration. It does, however, appear that the apparent discrepancy between the results obtained with different metals, or in different solutions, and the apparent conflict between short-period and long-period experiments are capable of explanation, and that, viewed broadly, all the facts established appear to form part of the same general scheme of things.

## PART II.—DESCRIPTION OF THE RESEARCH.

By R. S. THORNHILL, PH.D.

The experiments described below include :

A.—Qualitative experiments in which heat was communicated to various waters, including waters treated with inhibitor, through a metal strip heated at one end. The purpose of these experiments was to discover whether water treated with magnesium chromate after rusting had commenced, or at intervals insufficient to prevent attack altogether, perforated steel more quickly or less quickly than untreated water.

B.—Quantitative experiments to discover whether in cold undisturbed solutions the addition of increasing amounts of magnesium chromate to Cambridge tap water or potassium

<sup>1</sup> U. R. Evans, *Journal of the Chemical Society*, 1929, p. 115.

<sup>2</sup> T. P. Hoar, *Transactions of the Faraday Society*, 1937, vol. 33, p. 1152.

chloride solution produced an intensification of attack and accelerated thinning. This led on to experiments dealing with additions of chromate, carbonate and vanadate, designed to clear up the causes of water-line attack.

C.—Quantitative experiments to discover how the treatment of water with magnesium chromate affected the heat transfer and how it compared with softening in this respect.

#### A.—Experiments with Alternate Heating and Cooling.

Carried out by A. SHADBOLT.

*Experimental Procedure.*—The metal strips through which the heat was conveyed to the liquid measured 6 in.  $\times$  1 in., the thickness being 0.014 in. (0.36 mm.). They were cut from sheets of South Wales steel *M*, the analysis of which is shown in Table I.

TABLE I.—Analyses of the Materials.

	Steel <i>M</i> .	Ferrottype.
Carbon . . . . .	0.13%	0.115
Manganese . . . . .	0.35%	0.350
Silicon . . . . .	0.01%	0.045
Sulphur . . . . .	0.061%	0.020
Phosphorus . . . . .	0.060%	0.072
Copper . . . . .	0.08%	Trace
Chromium . . . . .	...	0.050

One end of a strip extended over a Bunsen flame and the other end was bent over into the glass vessel which contained the liquid; this vessel was protected from direct radiation from the flame by

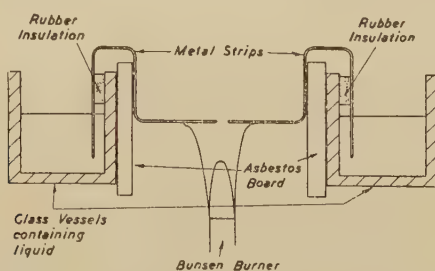


FIG. 1.—Apparatus for the Study of Corrosion with Heat introduced along Steel Specimens.

interposing a square of asbestos board. Three such units (two of which are shown in Fig. 1) were arranged round each burner. There was about 30 c.c. of liquid in each vessel, sufficient in fact to cover

a square inch of steel. Heat was supplied at such a rate that the water was raised to 50° C. in half an hour; at the end of this period the burner was turned out and the whole apparatus allowed to cool naturally. This heating and cooling sequence was termed a *cycle*, and was repeated at an average of about four cycles each day. Distilled water was added daily to replace evaporation.

Preliminary experiments were carried out with unabraded material cut from the centre of the sheet, which was free from visible scale. The waters tested comprised :

- (1) Cambridge fully softened water,
- (2) Cambridge raw water,
- (3) Cambridge raw water containing 3% of  $M/2$  magnesium chromate (without excess of magnesia).

As shown in Table II., the unsoftened water is rich in calcium bicarbonate, whilst softening, being carried out by the base-exchange process, has largely replaced this by sodium bicarbonate.

TABLE II.—*Typical Analyses of Waters used in Principal Experiments.*

(Parts per 100,000.)

	Cambridge Raw Water.	Cambridge Fully Softened Water.	Cambridge (Blended) Tap Water.	London.	Sheffield.
Calcium . . . . .	9.20	Nil	3.75	10.0	1.03
Magnesium . . . . .	0.14	Nil	Nil	0.54	0.37
Sodium . . . . .	0.80	11.64	4.87	?	0.80
CO <sub>3</sub> . . . . .	12.0	12.0	12.0	?	0.46
SO <sub>4</sub> . . . . .	1.4	1.4	1.4	3.6	2.76
Chlorine . . . . .	1.3	1.3	1.3	2.5	1.33
NO <sub>3</sub> . . . . .	2.5	2.5	2.5	?	0.44
Silica . . . . .	1.4	1.4	1.4	?	0.39
“Free” CO <sub>2</sub> . . . . .	1.8	Nil	1.8	Nil	?
Total alkalinity as CaCO <sub>3</sub> . . . . .	20.0	22.0	20.0	?	0.76
pH value . . . . .	7.3	8.3	7.3	?	6.9
Temporary hardness . . . . .	18.0	Nil	14.0	21.5	0.7
Permanent hardness . . . . .	5.0	Nil	Nil	4.5	3.4

After 60 cycles there was no corrosion in the water containing magnesium chromate, although the untreated water had begun to produce rust after the first cycle. The same result was obtained in 30-cycle experiments with waters from Sheffield, London and Birmingham.

In the main series of experiments, the conditions were more severe. In addition to bright specimens, another set received a preliminary rusting by subjection to four cycles in water free from inhibitor, the purpose being to discover whether magnesium chromate would arrest corrosion which was already well advanced. In a third set of specimens, conditions were chosen favourable to

the production of intense corrosion at a scratch-line through a scale-covered surface; strips were cut from the marginal portions of the sheets (which always carried scale), and three vertical lines were ruled through the scale by means of the Mears-Ward scratch machine.<sup>1</sup>

The waters tested were the same as in the preliminary experiments, except that the magnesium chromate contained excess of magnesia and was prepared *in situ* by mixing 1.0 c.c. of a suspension of magnesia ( $\text{MgO}$ , 40 g. per litre) and 0.5 c.c. of chromic acid ( $\text{CrO}_3$ , 100 g. per litre) to every 28.5 c.c. of water. This mixture was termed the "unit dose" and was added to the appropriate waters after certain specified numbers of cycles had been performed; the two reagents were present in the proportion  $2\text{MgO}:\text{CrO}_3$ , so that the mixture may be termed *basic magnesium chromate*. (The magnesia and chromic acid should be added separately, and the water is cloudy after treatment, owing to the excess of magnesia.)

The three types of specimen (bright, rusty and scaly) were tested in vessels 1, 2 and 3 which contained unsoftened water and one unit dose. At the end of 60 cycles it was noted that rust was beginning to appear on all three specimens, indicating that the inhibitor was ceasing to be effective (perhaps through local exhaustion); accordingly, another unit dose was added, and so on at the end of every succeeding 60th cycle. This procedure was termed "*full replenishment*." Vessels 4 and 5 served to show the behaviour of bright and scaly steel in unsoftened water without inhibitor, whilst vessel 6 contained a bright steel specimen in softened water initially containing one unit dose, further unit doses being added every 120th cycle; this plan of adding doses at intervals twice as long as those needed to keep pace with rusting was called "*stinted replenishment*."

Vessels 7 to 12 comprised an analogous series of experiments exactly similar, except that they contained tap water acidified by saturating with carbon dioxide. Owing to the more corrosive nature of the acidified water, it was necessary to add the second unit dose much earlier, *i.e.*, at the end of the 26th or 29th cycle in different cases. Here "*stinted replenishment*" signifies additions every 58th cycle.

*Results.*—The observations are summarised in Table III., which shows the number of cycles elapsing before (1) the first appearance of rust, (2) the first appearance of white deposit, and (3) perforation or breaking. As expected, perforation occurred earlier on the scaly than on the bright specimens, doubtless owing to the large cathode-anode ratio; it is significant that perforation occurred on the scratch-lines. The number of cycles required for perforation was actually less in raw water than in acidified tap water; this is believed to be due to the fact that in the acid water the area of attack spread

<sup>1</sup> R. B. Mears and E. D. Ward, *Journal of the Society of Chemical Industry*, 1934, vol. 53, p. 382r.



TABLE III.—*Experiments with Alternate Heating and Cooling.*

Specimen No.	Surface Condition.	Treatment.	Cycles at which—				Appearance of Specimen after Conclusion of Experiment.
			Unit Dose Added.	Rust first Observed.	White Deposit first Observed.	Perforation or Breakage occurred.	
<i>Raw Water.</i>							
1	Bright	Full replenishment	1, 60 and then every 60th to the 520th	59th	306th	{ Not perforated at 520th  Broke at 520th  Perforated at 395th, broke at 473rd  Not perforated at 520th	Some white deposit on specimen. Only one rust spot. Some deposit on specimen; rust spot on one scratch-line. Part of immersed area, originally rusty, now covered with white deposit. Breakage above water-level. Most of rust on specimen around edges. Three points of perforation on scratch-lines, another at edge. Breakage above water-level. No appreciable thinning. White deposit on specimen.
2	Sealy		...	1st	...		
3	Rusty		...	1st	...		
4	Bright	{ No inhibitor	...	...	...		
5	Sealy		...	...	...		
6	Bright	Stinted replenishment	1, 120 and then every 120th to 520th	60th	212th		
<i>Acidified Tap Water.</i>							
7	Bright	{ Full replenishment  No inhibitor	1, 26 and then every 26th to 612th	25th	273rd	{ Not perforated at 612th  Not perforated at 612th  Perforated at 448th, broke at 542nd  Not perforated at 612th	Free from deposit on constantly immersed portion. Very rusty. Perforation at scratch-lines. Very rusty. Breakage above water-level. No appreciable thinning. Slight deposit on immersed portion.
8	Sealy		...	1st	...		
9	Rusty		...	1st	...		
10	Bright		...	29th	212th		
11	Sealy						
12	Bright	Stinted replenishment	1, 58 and then every 58th to 612th				

out more quickly, so that the rate of perforation was somewhat diminished. In waters treated with basic magnesium chromate, with full replenishment, practically no rusting occurred; there was, however, deposition of white material, both on the immersed part of the specimen and at the bottom of the vessel.

Summarising the results, we may note :

(1) Addition of basic magnesium chromate every  $n$ th cycle (where  $n$  is the number of cycles required for rusting to appear in a solution originally containing one unit dose) is sufficient to prevent the extension of the rust, and in long-continued experiments may completely obliterate it, possibly by subsequent deposition of chalky matter.

(2) Where a specimen has already started to rust before the addition of basic magnesium chromate, the addition stops the rusting.

(3) Even stinted replenishment of this inhibitor (*i.e.*, additions every  $2n$  cycles) prevents perceptible thinning in a period sufficient to produce actual perforation in the untreated water. Under these conditions, therefore, basic magnesium chromate may be regarded as a "safe" inhibitor.

(4) Although basic magnesium chromate prevents serious corrosion under conditions of full and stinted replenishment, it does not indefinitely prevent the deposition on the heated surface of chalky matter from raw water.

### B.—*Experiments in Unheated Stagnant Liquids.*

Five sets of experiments, which are summarised in Table IV., have been carried out. These fall into two main groups.

#### (a) *Experiments with Chromates and Vanadates.*

*Experimental Procedure.*—The material used in series 1 to 4 was again steel  $M$ , abraded with Oakey's blue-back emery cloth No. 1 and cut up into strips measuring  $\frac{3}{4}$  in.  $\times$   $2\frac{1}{2}$  in. These were then degreased with dry acetone and stored in a desiccator until required. Some of the specimens used in series 1 were oxidised (*a*) by heating in an electric furnace for 5 min. at  $350^{\circ}$  C. to the first-order blue tint, and (*b*) by heating in a Bunsen flame until covered with a thick grey oxide film. The specimens shown as "scratched" in Table IV. were engraved with a single vertical line passing through the level of the water-line; this was applied by the Mears-Ward machine. The mixtures of inhibitor and corrosive solution were prepared from the following stock solutions: Potassium chromate ( $M/5$  and  $2M$ ); sodium vanadate ( $M/5$  and  $M$ ); sodium carbonate ( $N$ ); potassium chloride ( $M/5$ ); and Cambridge tap water. Magnesium chromate was added from two stock solutions, as in Section A, and always in the proportion  $2MgO : CrO_3$ .

The specimens were immersed at an angle of about  $60^{\circ}$  to the

TABLE IV.—*Classification of Experiments without Heating.*

Series.	Number of Specimens.	Inhibitor.	Corrosive Solution.	Surface.	If Scratched.	Distinguishing Features of the Series.	Scope of Experiment.
1 <i>a</i>	24	Magnesium chromate	Tap water	$\left. \begin{array}{l} a \text{ and } c \text{ abraded,} \\ \text{furnace and} \\ \text{flame tinted,} \\ b \text{ and } d \\ \text{abraded only.} \end{array} \right\}$	Yes, all specimens	KCl decreases in concentration as inhibitor increases. Mixtures prepared from stock solutions, total volume being 40 c.c.	Maximum depth of penetration, and descriptive.
<i>b</i>	18	Potassium chromate	Tap water				
<i>c</i>	40	Magnesium chromate	KCl				
<i>d</i>	17	Potassium chromate	KCl				
2	21	Potassium chromate	KCl	Abraded	No	KCl concentration constant, $M/10$	As above.
3	21	Potassium chromate	KCl	Abraded	No	As above, but metal wetted above the water-line	Descriptive.
4	20	Sodium vanadate	KCl	Abraded	No	As above	Maximum depth of penetration, and descriptive.
5	28	Sodium carbonate	KCl, and carbonate alone	Abraded	No	Variable ratios of carbonate to chloride and variable total concentration. Also varying concentrations of $\text{Na}_2\text{CO}_3$ alone	Descriptive.

horizontal in small glass jars; these were placed in a metal cabinet with a glass front which permitted observations to be made on the progress of corrosion whilst maintaining a fairly saturated atmosphere inside; by this means changes in the water level were much reduced.<sup>1</sup> As a guide, a parallel set of experiments was started under a large bell-jar, from which specimens were removed at various intervals for inspection. After 60 days it was decided that corrosion had gone far enough to permit a comparative estimate to be made of the depth of penetration, and the main series were then wound up. The rust which had formed was quite loose and was washed off into the vessel with hot water, and the specimen was dried on filter paper. The amount of iron in the corrosion product collected in the vessel was determined by the standard method with potassium dichromate solution, using barium diphenylamine sulphonate as indicator.<sup>2</sup>

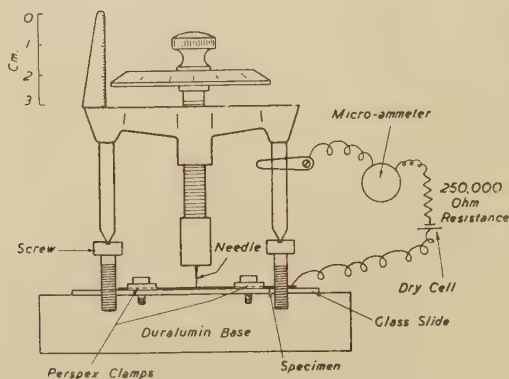


FIG. 2.—Apparatus for Measuring the Loss of Thickness.

The depth to which corrosion had penetrated was determined by means of the instrument shown in Fig. 2. A conventional spherometer was mounted on three large screws set into a base-plate of Duralumin, thus enabling a small attachment bearing a needle point to be fixed to the adjustable screw. The specimen was clamped down on to the base-plate by two Perspex strips, but it was possible to move it about so as to bring any desired spot under the needle point. In order to indicate exactly when contact

<sup>1</sup> It was originally intended to pass saturated air through the cabinet, and Dr. W. H. J. Vernon kindly provided some valued advice on this matter. It was later found that the water level remained sensibly constant without special precaution, and consequently the plans were not put into effect during the research described. Extra vessels containing water were introduced into the cabinet.

<sup>2</sup> See, for instance, D. Stockdale and J. Dexter, "Clowes and Coleman's Quantitative Chemical Analysis," p. 165. London, 1938: J. and A. Churchill, Ltd.



had been made, a 1.5-V. dry cell, micro-ammeter and  $\frac{1}{4}$ -megohm resistance were connected across the needle and specimen. In taking readings, the centre screw was rotated until electrical contact was made with the specimen, either (a) on the unimmersed portion and then on the immersed portions or (b) around a pit or depression and then in the depression itself. The difference between the mean reading on the unattacked metal and the greatest reading on the corroded part was taken as the depth of penetration. The results are given in terms of divisions where one division equals 0.005 mm.; a difference of 0.002 mm. could be detected. The thickness of the specimens (0.33 mm.) corresponds to about 66 divisions.

With the exception of those specimens in ordinary tap water and potassium chloride, the distribution of corrosion on the two sides of the specimen is different. In general the greatest pits, and those which have been measured and included in the following Tables, were found to occur on the upper side of the metal; these represent the depth of penetration from one side only. The greatest possible depth is the thickness of the specimen. In solutions free from inhibitor, where the corrosion is well spread out, there is a general thinning of the specimen; the spherometer measures this diminution of thickness, and hence, on the assumption that had one side been protected from corrosion the thinning would have been halved, the depth of penetration for these specimens has been obtained from the diminution of thickness by dividing by two. (Even if this process of "halving" is considered wrong, the conclusions drawn below are not affected.)

*Results.*—Tables V. to IX. show the depths of penetration and weights of corrosion product for the various series.

TABLE V.—*Magnesium-Chromate/KCl Series. Three Types of Surface.*

Concentration of $\text{CrO}_3$ , Moles. per Litre.	Concentration of $\text{KCl}$ , Moles. per Litre.	Abraded Surface.		Flame-Tinted Surface.		Furnace-Tinted Surface.	
		Maximum Depth of Penetration, Divisions.	Iron in Corrosion Product, Mg.	Maximum Depth of Penetration, Divisions.	Iron in Corrosion Product, Mg.	Maximum Depth of Penetration, Divisions.	Iron in Corrosion Product, Mg.
0	0.2	8	221.3	22	326.4	7	397.2
0.0025	0.1985	28.5	24.4	40	21.7	16	44.0
0.00625	0.1965	29.5	15.9	12	24.7	45	38.2
0.0125	0.1925	21	27.6	26.5	47.8	17.8	32.6
0.025	0.185	28.5	25.7	22	61.2	19	7.2
0.050	0.17	7	12.5	13	9.1	13	23.8
0.075	0.155	6.5	22.2	20	6.8	11	9.2
0.10	0.14	25.5	5.7	15.5	1.7	18	7.0
0.15	0.11	0	2.0	7.5	1.6	20.5	4.1
0.20	0.08	0	3.6	3	0.8	8.5	0.9
0.25	0.05	0	1.2	4	0.9	0	1

TABLE VI.—*Magnesium-Chromate/Tap-Water Series. Three Types of Surface.*

Concentration of $\text{CrO}_3$ . Mols. per Litre.	Abraded Surface.		Flame-Tinted Surface.		Furnace-Tinted Surface.	
	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.
0	4.5	138.2	7.2	92	8.5	116.2
0.000625	4.8	2.9	21.5	1.7	18	1.1
0.00125	0	4.6	21.3	0.6	11	1.8
0.00250	28.5	4.6	2.5	1.1	2	0.5
0.00625	0	0.5	0	<1	0	<1
0.0125	0	0	1	<1	0	<1
0.025	0	0	0	<1	0	0
0.0375	0	0	0	<1	0	0

TABLE VII.—*Potassium-Chromate/KCl Series. Abraded Surface.*

Concentration of $\text{CrO}_3$ . Mols. per Litre.	Concentration of KCl. Mols. per Litre.	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.
0	0.2	8	221.3
0.0010	0.199	9	162.1
0.0025	0.1975	0 or 66 according as one rejects or includes the corners	31.7
0.005	0.195	10	38.0
0.0085	0.1915	16.5	38.4
0.0125	0.1875	6.5	31.5
0.025	0.175	8.0	21.1
0.050	0.15	22.0	13.4
0.10	0.10	25.0	14.6
0.15	0.05	27.0	14.9

In discussing the results, particularly where corrosion has occurred in or near the water-line, it is convenient to adopt the nomenclature of a previous paper.<sup>1</sup> Here the junction of air, liquid and metal has been termed the *meniscus head* (M.H.). The level where the prolongation of the horizontal surface of the liquid meets the metal is called the *meniscus foot* (M.F.). The intervening space is referred to as the *meniscus zone* (M.Z.).

Tables V. to IX. clearly indicate that, although the *total* corrosion is *diminished* by adding chromates to the solution, the *depth of penetration* is *almost always increased by very small amounts of inhibitor*. It should be emphasised that the intensified corrosion and/or pitting occurs when the amount of inhibitor is insufficient

<sup>1</sup> R. S. Thornhill and U. R. Evans, *Journal of the Chemical Society*, 1938, p. 2109.

TABLE VIII.—*Potassium-Chromate/Tap-Water Series. Abraded Surface.*

Concentration of $\text{CrO}_3$ . Mols. per Litre.	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.
0	5.5	129.9
0.0005	19.0	7.3
0.0010	10.5	4.6
0.0025	16	1.2
0.005	0	0
0.010	0	0
0.015	0	0
0.020	0	0
0.030	0	0

TABLE IX.—*Potassium-Chromate and Sodium-Vanadate/Constant-Chloride (M/10) Series. Abraded Specimens.*

Concentration of Inhibitor. Mols. per Litre.	Potassium Chromate.		Sodium Vanadate.* Maximum Depth of Penetration. Divisions.
	Maximum Depth of Penetration. Divisions.	Iron in Corrosion Product. Mg.	
0	9.8	249	5.7
0.0005	11.7	137	12.1
0.0010	33.5	83.6	9.4
0.0015	} 0 or 66 (corners corroded away) }	34.8	6.5
0.0020		23.9	9.6
0.0025		24.4	10.6
0.00375		25.0	7.8
0.0050		34.9	32.4
0.0085		28.2	37.7
0.0125	29.5	34.9	41.3
0.025	23.5	26.8	45.5
			(perforation)
0.0375	13.5	11.6	41.5
0.050	40	15.3	37.0
0.075	15.5	9.7	32.4
0.10	20	—	33
0.15	...	...	40
0.200	10	3.5	44.8
0.300	28.5	9.1	16.5
0.40	18.3	—	23.5
0.50	...	...	16.9
0.60	19.5	2.7	—
0.80	6.5	0.8	—
1.00	13	2.1	—

\* NOTE :—The iron in the corrosion product was not determined in the vanadate experiments. A dash in the other columns means that no determination was carried out.

to prevent attack completely. Basic magnesium chromate—just like potassium chromate or sodium vanadate—belongs to the dangerous class of inhibitors under these conditions.

In certain cases corrosion is largely of the pitting type, for instance, in vanadate-treated solutions at certain ranges of concentration; Fig. 3 shows the gradual passage from (1) general corrosion, through (2) localised corrosion, (3) water-line attack, and (4) pitting, to (5) practical immunity, as the vanadate concentration is increased. In other cases—notably where potassium chromate has been used as inhibitor—the area may be fairly extensive yet deeply corroded. In some instances where corrosion is in the water-line, filaments of corrosion product have stretched out and formed “boxes” on the sides of the vessels. Breakdown may occur at either the M.H. or M.F. If the soluble iron salts are not immediately precipitated, but can diffuse a short distance to the air/liquid interface, they may be oxidised and precipitated there, giving a thin film or membrane. If this grows and extends far enough up the curved surface of the meniscus to meet the metal, shielding off a portion of the metallic surface from oxygen, intensive corrosion results. In potassium chloride containing very little chromate deeply corroded areas have been noted, occasionally with abraded specimens, and frequently with tinted specimens carrying scratch-lines; the corrosion started at the M.F., gave rise to a film on the surface of the liquid, and eventually formed a box.

An interesting phenomenon has been noticed in certain chromate-chloride mixtures richer in chromate than those just mentioned. Breakdown often commences where the cut edges of a specimen pass through the water surface. A curved rust membrane appears in a plane which is roughly vertical but is concave towards the point on the edge where the corrosion has started; this rust membrane occupies the whole of the cross-section of the meniscus “triangle.” Shortly afterwards—probably because the inhibitor has become exhausted just outside the membrane (by keeping the latter in repair)—corrosion starts in the M.Z. just beyond the first membrane, and a second curved membrane appears outside the first and roughly concentric with it. This is followed by a succession of roughly concentric membranes, until the whole M.Z. is suffering corrosion. The union of these curved membranes goes to produce the familiar box of triangular cross-section, and a ribbed structure, marking the original sites of the curved membranes, remains visible at an advanced state of corrosion. The membranes recall the multiple mantles observed in other examples of extending corrosion,<sup>1</sup> except that their plane is roughly vertical instead of roughly horizontal. These triangular boxes usually lead to attack far more virulent than the roughly hemispherical blisters formed at susceptible points lower down.

Another cause of water-line attack was noted in certain liquids

<sup>1</sup> U. R. Evans, *Industrial and Engineering Chemistry*, 1925, vol. 17, p. 368.



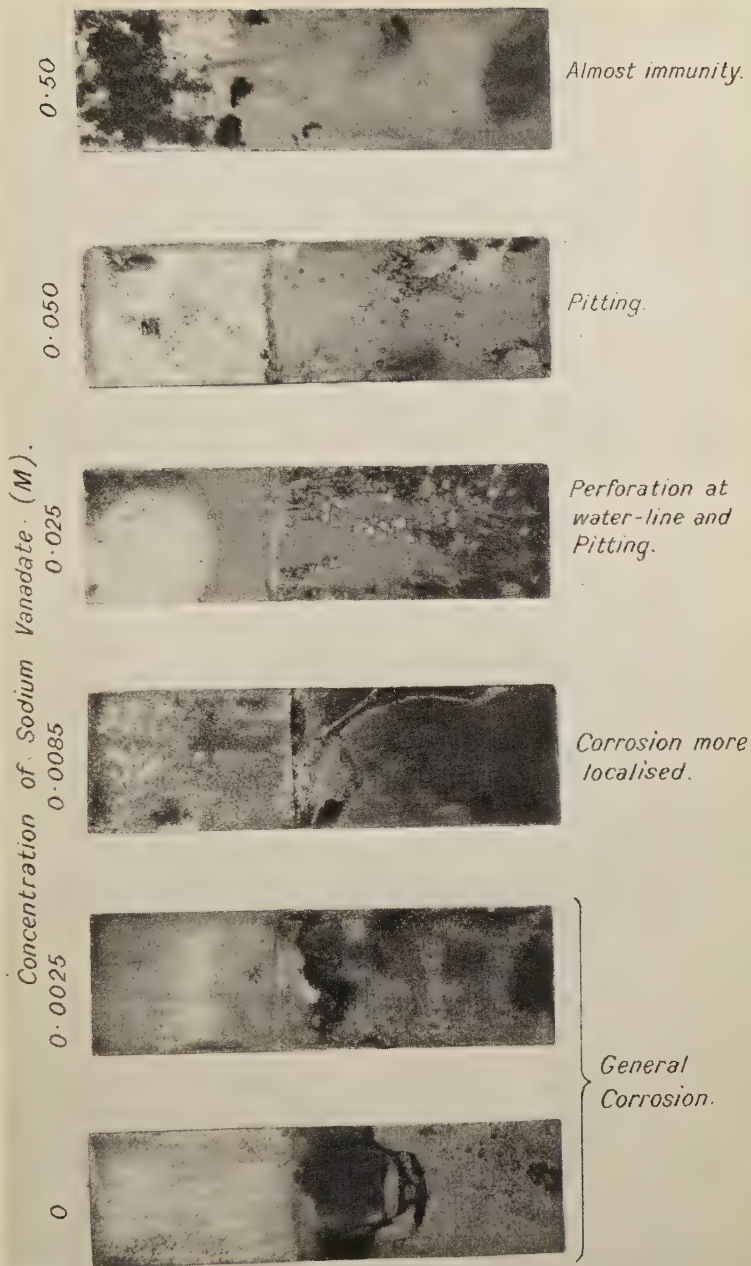


FIG. 3.—Effect on the Corrosion of Steel in 0.1M Potassium Chloride of adding Increasing Amounts of Sodium Vanadate.



of intermediate chromate concentration. Where moisture condensed above the water level it produced a little harmless rusting and then trickled down; at the water-line the inhibitor was locally diluted, and the cell:

Iron | Diluted inhibitor | Concentrated inhibitor | Iron,

with its small anode and large cathode, led to intense attack. This could only occur in a confined situation under conditions of unequal temperature, but such a state of affairs is not unlikely to occur during shut-down periods in the interior of some cooling systems, where an air-space exists above the liquid.

Further details of the distribution of corrosion are given in an Appendix.

(b) *Experiments with Sodium Carbonate.*

These experiments were carried out on ferrotype iron, of composition given in Table I., which was abraded and cut up into strips measuring 3 in.  $\times$   $\frac{3}{4}$  in. Four series of solutions were made up in which the ratios of carbonate to chloride were respectively 4:0, 3:1, 2:2, 1:3; each series comprised four sodium ion concentrations, namely,  $N$ ,  $N/10$ ,  $N/100$  and  $N/1000$ . It was interesting to find that those solutions rich in total sodium gave water-line attack, whilst those poor in sodium gave water-line immunity. This suggested that sodium carbonate alone might produce water-line corrosion if the concentration was suitably adjusted. Experiments showed this to be the case with concentrations lying between  $0.16N$  and  $0.03N$ . In about  $N/1000$  sodium carbonate water-line immunity was obtained; then as the concentration was increased to  $N/100$  a band of corrosion appeared at the M.F.; as the solution was made stronger in sodium carbonate the corroded area rose further into the water-line zone. As the concentration was increased to  $0.016N$  the band of corrosion approached the M.H. until it coincided with it, and then, as the concentration was further increased, the band decreased in width and finally disappeared entirely. Thus water-line corrosion can be obtained by sodium carbonate alone; the effect of adding chloride to carbonate solutions is to broaden the critical range of concentration and displace it to higher values.

The mechanism by which the box develops seems to be essentially similar to that observed with chromate solutions. If a number of drops of carbonate solution are placed on abraded steel and if the concentration lies within the critical range, it can be seen that those points of breakdown in the centre of the drop merely develop a green corrosion product, and corrosion does not become intense. Only rarely are breakdowns seen on the periphery of the drop; mostly they begin about 1 mm. from the edge, and as the corrosion product diffuses away it becomes oxidised at the surface of the drop, forming a membrane and a box; corrosion within the box is then intense, doubtless owing

to the combination of small anode and large cathode. The position of the interface with respect to the starting point of the corrosion seems to be important. Thus, in another experiment, a number of mild-steel rods  $\frac{1}{4}$  in. in dia. were waxed about half-way down and immersed in a solution consisting of 25 c.c. of normal sodium chloride, 25 c.c. of normal sodium carbonate and 450 c.c. of water. It was arranged that the horizontal boundary of the wax should lie (a) at the M.H., (b) at the M.F. and (c) a millimetre below the M.F. In the first two cases typical water-line breakdown was produced, but in the third case, although breakdown occurred at the wax boundary, corrosion did not develop beyond the formation of small rust blisters. This supports the view of water-line attack developed above.

### C.—*Influence of Inhibitors on Heat Transfer.*

In most measurements of heat transfer, "forced convection" is used; a liquid at temperature  $\theta_1$  may be forced by means of a pump at a definite velocity through a tube surrounded by liquid at a lower temperature  $\theta_2$ , and the fall in temperature is determined. To obtain absolute results this is the best method, but to obtain comparative results (as in studying the effect of an obstructive layer of scale or rust on heat transfer) a "free convection" method is suitable; here a metal tube containing liquid at  $\theta_1$  is placed in a vessel containing liquid at  $\theta_2$ , and the time taken for a thermometer situated centrally in the tube to fall to an intermediate temperature  $\theta_3$  is measured. Any obstructive film on the tube surface will show itself by an increase in the time needed, and the obstruction will not only act by directly interfering with the heat transfer, but also indirectly, because the convection will be slower with the slower temperature change, so that the layer of stagnant liquid—which furnishes an additional obstruction to heat transfer—is also increased. It is, of course, important that, in comparative experiments, the shape of the different tubes and the positions of the thermometers shall be identical; if this precaution be observed, very simple apparatus will suffice.

*Experimental Procedure.*—Three series of experiments have been carried out, illustrating the following conditions :

*Series 1.*—Heat transfer through vertical walls, but with a relatively small access of oxygen to the water, so that the rust was mainly of the magnetite variety.

*Series 2.*—Heat transfer through vertical walls with easy access of oxygen, so that yellow (ferric) rust was formed.

*Series 3.*—Heat transfer through horizontal walls on which rust sludge may settle as the corrosion proceeds.

Experiments in series 1 and 2 were carried out with small tubes which were constructed from steel *M* by wrapping a rectangle of material around a  $\frac{1}{2}$ -in. rod and soldering the edges. The tube



(Fig. 4(a)) so made was 3 in. in length and  $\frac{1}{2}$  in. in dia., and had a flange about  $\frac{1}{4}$  in. wide down the side. Running down the axis of the tube was a thermometer, which fitted securely into a rubber bung at the lower end and into a cork at the upper end. This ensured that the thermometer was centrally disposed with respect to the heating surfaces, and in so far as the geometry of the arrangement was concerned any circulation of water due to convection would be the same for all tubes. There were six tubes in each set of experiments, since the following three waters were represented in duplicate : (1) Cambridge raw water, (2) Cambridge raw water containing

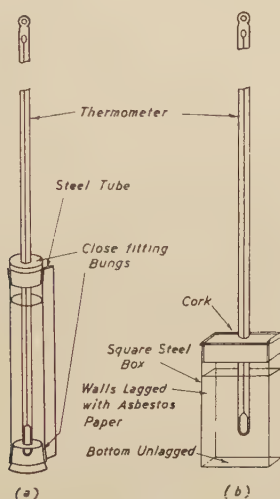


FIG. 4.—Apparatus for the Study of Heat Transfer (a) through vertical walls, (b) through a horizontal bottom.

inhibitor (1 unit dose per 30 c.c.) and (3) fully softened Cambridge water.

In series 1 a tube containing the water under examination was heated to 90° C. in a beaker of dilute potassium chromate solution, to prevent rusting of the outer wall, and was then transferred to a large vessel of water at 15° C. and immersed up to a line on the outside marking the level of the water inside. The time was observed during which the thermometer fell from 60° to 40° C., this temperature interval having been decided upon after previous trials. When 40° C. had been reached the tubes were taken out, dried and kept at room temperature until the next measurement, of which three were made each day. At night after the last reading the tubes were carefully emptied, so as to avoid disturbance of the rust adhering to the walls, and refilled to a constant level with the

appropriate water; during the night they were kept in a thermostat-room at 25° C.

The rust formed in series 1 was not fully oxidised and not adherent. In order to obtain a better oxygen supply, it was arranged in series 2 that the corroding liquid should be on the outside of the tube and the chromate solution on the inside. Taking the case of the softened water as an example, the appropriate tube was heated to 75° C. in a boiling tube containing about 20 c.c. of softened water and then immersed in a vessel containing 2 litres, also of softened water, at 15° C. Observations were made of the time needed for the temperature to fall from 60° to 40° C. During the rest of the day and night the tube remained in the large vessel of softened water, so as to become increasingly rusty. The same procedure applied to the raw and inhibited raw water. The chromate solution inside the tube was restored to its original level by additions of distilled water every morning.

A feature of series 1 and 2 was that a continually thickening layer of rust on the metal was not obtained; possibly the rust was precipitated at a distance from the metal and thus failed to adhere. In the third series of experiments it was arranged that rust from the side walls should collect on the surface through which the heat was being communicated. The vessels in this case were of square 1 in.  $\times$  1-in. cross-section and 2 in. deep (Fig. 4(b)), and were again fashioned from steel *M*. Direct passage of heat through the side walls was prevented by covering them with asbestos paper, using a polystyrene adhesive, the bottom being left uncovered. The thermometer was held in position by a square cork with the bulb  $\frac{3}{4}$  in. from the bottom of the box. Each water was tested in duplicate with 20 c.c. in each box. The height of each level was accurately known, and every morning losses by evaporation were made up by addition of the appropriate water. In the first set of experiments, extending over 20 days, the boxes were kept at 25° C. when not in use, and measurements were made of the time needed for the temperature to *rise* from 30° C. to 40° C. when immersed in dilute potassium chromate solution at 70° C. Continuing this series during the next eight days the conditions were slightly altered, the time being recorded for the temperature to rise from 25° C. to 35° C., *i.e.*, from the moment of immersion; the purpose of the change was to take account of any effect due to rust being heated up and then circulated round. The results showed considerable scatter, which was at first attributed to a non-reproducible stirring motion of the hot chromate solution. An attempt was made to improve matters by letting the solution cool without stirring from about 73° C.; the only movement then possible was that due to convection currents. Readings under these conditions were continued for another 21 days, but the reproducibility was no better.

Altogether two thousand measurements of heat transfer were made.

*Results.*—A decrease in heat transfer is reflected in an increase in the time of heating or cooling. It is impossible to record all the results, but the diagrams are typical. The graphs of Figs. 5 and 6 show the day-to-day variation of time for the three series of experiments. In series 1 the heat transfer usually deteriorated over the week-end when the tubes were not disturbed and rust was given an opportunity of accumulating, but on Monday it improved again when normal working was recommenced. This applied to tubes containing raw and softened water, but in inhibited water the heat

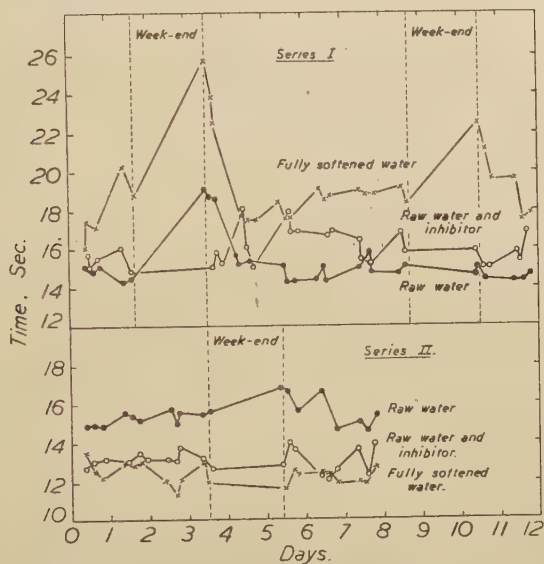


FIG. 5.—Study of Heat Transfer (a large value represents a low transfer rate).

transfer remained sensibly constant, since no rust or visible scale was formed. The heat transfer in series 1 was worse for the fully softened water than for raw water, doubtless owing to the greater amount of rust produced.

In series 2 the figures for all three waters remained largely unaltered, indicating that the heat transfer remained sensibly constant. This is understandable in view of the fact that most of the rust was falling off.

In series 3 (heating through a horizontal bottom) the times show a much greater scatter, but on the whole there seems to be a slight upwards tendency, at least in the raw water. Rust sludge certainly accumulated in those boxes without inhibitor, and magnesia from the make-up water when inhibitor was added. Nevertheless, the

fact that the rise in time of heating is so small indicates that heat continued to be communicated to the water without sensible retardation; one possible explanation is that the heat passed from the metal bottom to the vertical walls, and so reached the liquid.

To summarise the situation, it appears that heat transfer is not greatly affected by corrosion if the rust is non-adherent and is continually removed. Under these conditions the addition of

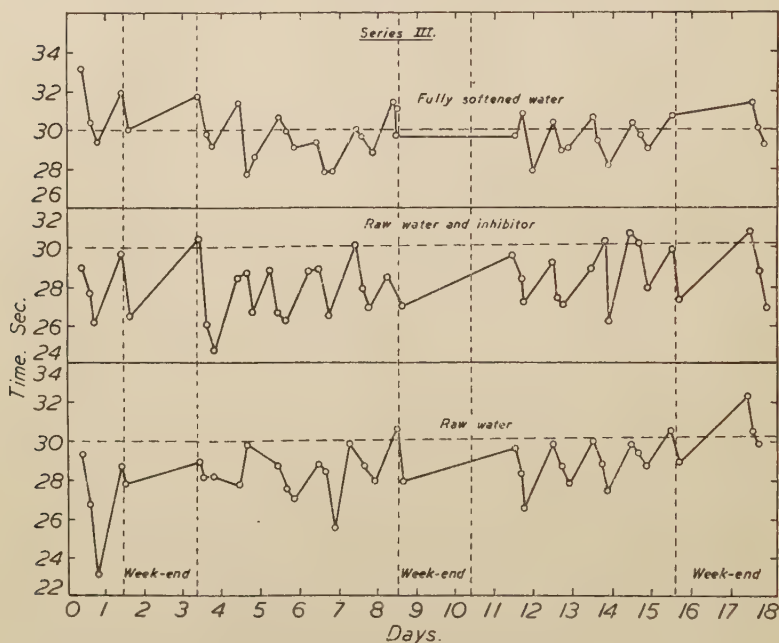


FIG. 6.—Study of Heat Transfer (a large value represents a low transfer rate).

a corrosion inhibitor would not materially affect the heat transfer. If loose rust settles on one portion of the heating surface, but heat can still be communicated to the liquid by an alternative route, the net rate of heat transfer would still seem to remain largely unaltered.

#### ACKNOWLEDGMENTS.

The authors wish to express their best thanks to the Corrosion Committee of The Iron and Steel Institute and The British Iron and Steel Federation, and particularly the Chairman, Dr. W. H. Hatfield, F.R.S., for their support and interest. They would



acknowledge also the fruitful results of discussion with Mr. E. W. Colbeck, Mr. P. Hamer and Mr. L. Powell, of Imperial Chemical Industries (Alkali), Ltd., who have been engaged on investigations into another group of inhibitors involving somewhat analogous problems; the photograph (Fig. 3) showing the types of attack with different quantities of inhibitor was taken in Mr. Colbeck's laboratory from a set of specimens produced at Cambridge. The investigation also owes much to the kindness of Mr. T. Henry Turner, Chief Chemist and Metallurgist of the London and North-Eastern Railway Company, and to Mr. P. Porteous, Engineer Manager and Secretary of the Cambridge University and Town Waterworks Company, who have kindly provided facilities for the supply of water samples and helped the work in other ways. The authors would thank Dr. T. P. Hoar and Dr. J. N. Agar for much fruitful advice during the research, and would particularly acknowledge the valuable services of Mr. A. Shadbolt in connection with the experiments of Section A.

APPENDIX.—*Distribution of Attack in Solutions Containing Inhibitors.*  
*Magnesium-Chromate/Potassium-Chloride Series.*

(a) *Abraded Specimens.*—In potassium chloride solutions the corrosion began at a point on the scratch-line some distance from the M.F. and spread downwards and sideways. The addition of a small quantity of chromate confined the corrosion to the scratch-line. At higher concentrations there appeared to be points of breakdown on the specimen above the M.H. which extended into the M.Z. and below. In high-chromate solutions corrosion was entirely inhibited.

(b) *Tinted Specimens.*—The addition of a small amount of chromate limited the corrosion to a few points along the scratch-line and a strongly etched zone beginning at the M.H. and extending a short distance downwards. Pitting along the scratch-line occurred over a wide range of inhibitor concentrations and was finally prevented. Colours in the M.Z. indicated that film breakdown and repair was occurring.

*Magnesium-Chromate/Tap-Water Series.*

*Abraded and Tinted Specimens.*—In tap water the meniscus alone was free from corrosion and was covered with a white film. A very small amount of inhibitor limited the corrosion to the scratch-line, but with a very definite box at the water-line. Larger concentrations completely suppressed the corrosion.

*Potassium-Chromate/Potassium-Chloride Series.*

*Abraded Specimens.*—In ordinary potassium chloride solutions the upper boundary of the corroded zone was in the shape of a W and was located well below the M.F. As the chromate concentration

was increased, four distinct corrosion patterns were obtained in turn:

- (1) Localised corrosion in pits along the scratch-line, but still on the immersed area.
- (2) Large etched areas with breakdown on the immersed part of the metal and in the M.H. itself.
- (3) Descending streamers of corrosion product ending on small centres of corrosion.
- (4) Immunity.

As the corrosion proceeded the chromate in the more dilute solutions became exhausted and the corrosion became more general. In some of the solutions stronger in chromate it was noticed that a corrosion spot *above* the M.H. might join up with a spot below it and thus give rise to considerable intensification. Even with the highest chromate concentration, protection was only temporary; after 14 days a breakdown occurred on the part of the metal above the M.H. and spread downwards into the M.Z.

#### *Potassium-Chromate/Tap-Water Series.*

*Abraded Specimens.*—In ordinary tap water the whole of the immersed area was corroded with the exception of the water-line zone, which bore a white deposit of chalk. When only a small amount of inhibitor was present the corrosion was confined to a descending zone starting from the M.F. and spreading out on each side of the scratch-line. With still more inhibitor the zone was contracted until there were only a few points along the scratch-line, and with still more chromate the attack was entirely inhibited.

#### *Potassium-Chromate/Constant-Chloride Series.*

*Abraded Specimens, Unscratched.*—On these specimens and on a similar series wetted above the water-line, four separate zones could be noted:

(1) A range of concentration from 0 to 0.0025*M* where the area of corrosion diminished with increasing amounts of chromate but was always located well below the M.F. Corrosion was very intense at the corners where the strips were in contact with the bottom of the beaker. The distribution of corrosion was not affected by wetting above the water-line.

(2) A range where breakdown in the M.Z. was particularly likely. Breakdown occurred at the cut edges or at any point along the M.H.; the probability of corrosion was greatly decreased by very careful immersion of the specimen at the beginning of the experiment and was increased by wetting the specimen above the water-line.

(3) A range in which the corrosion was entirely on the immersed zone and was characterised by descending black

streamers of corrosion product ending up on tightly massed rust spots.

(4) A range, which included the stronger solutions of inhibitor, in which there was no corrosion on the immersed area but breakdown on the part out of the liquid.

*Sodium-Vanadate/Constant-Chloride Series.*

*Abraded Specimens, Unscratched.*—Sodium vanadate is a much less effective inhibitor than the chromates and therefore, even with a considerable amount in solution, the distribution is well spread out. In the presence of 0.005*M* sodium vanadate a rust line appeared in the M.F., and in stronger solutions the rust line was definitely in the M.Z. but the rest of the specimen was free. In course of time this breakdown in the water-line developed into very well-defined boxes, which sent out shoots to the opposite side of the vessel. From about 0.025*M* the width of the box decreased; there was a great deal of rust hanging off the specimen in the form of "hairs," which when removed revealed some very deep pits. These increased in depth as the vanadate concentration increased. When a certain limit was reached, about 0.2*M*, the only corrosion apparent was on the creep zone, and the greater the concentration of sodium vanadate the more distant was the breakdown from the surface of the liquid.

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### CORRESPONDENCE.

Mr. P. HAMER and Mr. E. W. COLBECK (I.C.I. (Alkali), Ltd., Winnington) wrote: Apart from its very real contribution to our knowledge of corrosion and the mechanism of protection, this paper is particularly interesting and valuable, because the authors have deliberately designed certain of their experiments and apparatus to try and answer questions which have a direct application in industrial plant. We refer particularly to the heating and cooling experiments, to the heat-transfer experiments and to those in which the effects of the inhibitor on pre-rusted metal were studied. It may not always be possible under operating conditions to arrange for a continuous supply of inhibitor, and the experiments to study the effect of "stinted replenishment" are obviously of great practical importance.

To this series might well be added the question of cost, which is usually uppermost in the minds of plant engineers. For example, we know of recirculating systems in which corrosion has occurred

to the point of failure, and which take in fresh-water make-up to the extent of some 2000 gal. per hr. In such a system the cost of replacing the damaged tube may be only a very small proportion of the total loss incurred because the plant is not available. Both these items should be taken into account when considering the value of corrosion inhibition.

We should like to ask the authors' views on the probable cost of using magnesium chromate.

A second point which appears to us important is that it is not unusual to find slimes of vegetable or bacterial origin in recirculating cooling systems. It seems that these might profoundly modify the operation of any inhibitor, and, in fact, they can be so detrimental to heat transfer that chlorination is commonly used to destroy the growths. Chlorination may be continuous or intermittent, and some corrosion inhibitors, particularly those containing organic material, have a fairly high chlorine demand, so that the cost of continuous chlorination would be increased and indeed the effect of chlorine on the functioning of the inhibitor may not be beneficial.

We should like the authors' views in these points.

Finally, in a paper presented before the Electrochemical Society, New York, Chyżewski and Evans<sup>1</sup> pointed out that those inhibitors which act by blocking the anodic reaction may, if added in insufficient quantity, actually increase the "intensity of corrosion," *i.e.*, the attack per unit area of the part affected. The paper describes experiments by means of which inhibitors were divided into the anodic or cathodic class according to which reaction was most affected. By the technique described, it should be possible to decide whether any inhibitor is potentially "safe" or "dangerous."

We would like to know whether magnesium chromate or any of the other inhibitors used in the present paper have been tested by the methods described in the above-mentioned paper, and, if so, whether the classification obtained is supported by the evidence of the experiments described here.

### AUTHORS' REPLY.

The AUTHORS wrote in reply: We appreciate the communication from Mr. Hamer and Mr. Colbeck, who are in a position to judge of the factors which would determine the utility of an inhibitor in an industrial plant. Regarding the cost of application to a cooling system, this will, of course, depend on:

(1) The wholesale price of the chemicals used.

(2) The amount of water lost by *evaporation*, which will concentrate the chemical in the remainder, and *diminish* the amount which need be added in the "make-up."

<sup>1</sup> *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 215



(3) The amount of water lost by *leakage* or *spray*, which will carry its chemicals with it, and will *not affect* the amount needed in the make-up.

(4) The amount of chemical consumed in repairing protective films on the metal, or removed by organic growths or in other ways; this will *increase* the amount needed in the make-up.

Obviously, the total make-up comprises both (2) and (3), and further details are needed before the cost could be calculated in any given case. Actually, Mr. Hamer and Mr. Colbeck are far more favourably placed than we to compute the effect of factors (1), (2) and (3). Regarding (4), the removal of chemical will depend largely on the ratio of surface area to volume of the plant. Experiments would have to be made on the consumption of inhibitor with different ratios before any estimate of cost could be made, but these must be left until an inhibitor is found which would be satisfactory in other respects.

However, assuming that factor (2) exactly balances factor (4) (this is purely a guess), then the amount needed in the make-up to obtain the concentrations used in the laboratory experiments is 3 g. per litre. Taking the price of chromic acid as 168s. 8d. per cwt. and of "light magnesia" as 2s. 2d. per lb.,<sup>1</sup> the cost would work out at about one penny per gallon.

We agree that vegetable or bacterial matter—or the chlorides resulting from the chlorination needed to destroy it—would demand an increase in the amount of chromates; this is well known to be the case with potassium or sodium chromate, and a few figures on the subject are available.<sup>2</sup> It would be interesting to know whether, on grounds of cost, the use of formaldehyde instead of chlorine could be considered. We have not tested magnesium basic chromate in the Chyżewski-Evans, cell. We think, however, that, under practical conditions, it should retard both anodic and cathodic reactions.

<sup>1</sup> Provisional prices quoted by a well-known dealer; doubtless Mr. Hamer and Mr. Colbeck could obtain more advantageous terms.

<sup>2</sup> W. G. Kroenig and S. E. Pawlow, *Korrosion und Metallschutz*, 1933, vol. 9, p. 268 (especially p. 272). C. van Brunt and E. J. Remscheid, *General Electric Review*, 1936, vol. 39, p. 128.



## TESTS ON THE CORROSION OF BURIED FERROUS METALS.<sup>1</sup>

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*Paper No. 6/1942 of the Corrosion Committee (submitted by the Sub-Committee on the Corrosion of Buried Metals).*

### ABSTRACT.

This is an interim report on researches on the corrosion of buried metals conducted by the Corrosion Committee. The work is intended to precede the more extensive investigation contemplated by that Committee in collaboration with the Sub-Committee on Soil Corrosion of Metals of the Committee on Soil Corrosion of Metals and Cement Products of The Institution of Civil Engineers, who during the last year have made a grant in aid of the research.

Experiments on various irons and steels buried in clay soils at Binfield, near Wokingham, for three years are first described. The rate of general corrosion, even in these reputedly corrosive soils, was low, about 0.0015 in. per year, and, in agreement with previous tests in the United States, no appreciable differences were found in this rate for ordinary ferrous materials, *i.e.*, cast irons, structural steels and wrought irons. In particular, the presence of low percentages of copper and/or chromium in steel or wrought iron had no effect on their resistance to corrosion under these conditions.

Data have been obtained for the effects of depth of burial and other factors on the corrosion rate, which will be of value when arranging future tests. It is shown that the experimental error is greater in this type of test than for corrosion tests under other conditions of exposure and it is concluded that future tests should be made in triplicate at least.

Samples of soil from the exposure sites were subjected to chemical, physical and microbiological examination, but it was not found possible to correlate the results of the corrosion tests with any of the soil characteristics. Sulphate-reducing bacteria were present in appreciable numbers in all the samples except one.

Work is reported on a method of determining the relative corrosiveness of soils by following the change in the electrical resistance of buried coils of wire due to corrosion. It is demonstrated that it is practicable to determine the resistance in the soil itself and that this resistance increases proportionately to the corrosion. Although the results obtained may not be strictly representative of the behaviour of massive materials such as pipes, it is hoped that the method will prove a convenient means of comparing the corrosiveness of different soils.

The paper concludes with suggestions for a continuation of the work. It is suggested that this should mainly take the form of developing the electrical-resistance method of testing. Experiments

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<sup>1</sup> Received December 22, 1941.

to date have been artificially accelerated by electrolysis. It remains to be shown that the method will respond suitably to the slower changes due to corrosion under natural conditions in the soil, and to correlate determinations made in this way with the more usual loss-in-weight tests on massive specimens.

### A.—Introduction.

ALTHOUGH extensive researches on the corrosion of buried metals have been conducted in the United States by the National Bureau of Standards and to a lesser degree in the Netherlands by the Dutch Corrosion Committee, little systematic work in this field has been undertaken in Great Britain. The subject has, however, been under consideration for some time by the Sub-Committee on Soil Corrosion of Metals of the Committee on Soil Corrosion of Metals and Cement Products of The Institution of Civil Engineers, on which The Iron and Steel Institute Corrosion Committee and the British Non-Ferrous Metals Research Association are represented. In fact, shortly before the outbreak of war, a Panel of this Sub-Committee had drawn up an extensive programme of tests on both ferrous and non-ferrous metals and alloys which had been adopted by the Committee. This would have involved the provision and exposure of large amounts of representative materials at numerous exposure sites in Great Britain; in principle, The Institution of Civil Engineers would have been responsible for finance, whilst The Iron and Steel Institute and the British Non-Ferrous Metals Research Association would have supplied the specimens required for the tests and undertaken the experimental work. It was clearly necessary to postpone the execution of this programme until circumstances were more propitious, but it was decided to undertake immediately certain preliminary experimental work to pave the way for the major research.

The conduct of this preliminary work has been greatly facilitated by a financial grant by The Institution of Civil Engineers to the Corrosion Committee, which is acknowledged with appreciation. The present paper is intended to cover the results obtained during the first year of this initial investigation. This has been devoted to a detailed examination of a series of specimens of various irons and steels that had been buried in a number of clay soils at Binfield for three years and to investigating whether the corrosion of a buried metallic specimen can be determined without removing it from the soil by measuring the change in its electrical resistance.

Considerable assistance has been rendered by several iron and steel firms in supplying materials for test, and due acknowledgment will be made in the text. Particular reference should be made here to the practical assistance rendered by the Mid-Wessex Water Company and their Managing Director, Mr. Claude Pain, M.Inst.C.E., who generously provided the necessary exposure sites at Binfield and the labour incidental to burying and unearthing the specimens.



Mr. H. J. Bunker, of the Chemical Research Laboratory, Teddington, and Dr. E. W. Russell, of the Rothamsted Experimental Station, have also given valuable help in connection with the bacteriological and analytical examination of soil samples, respectively.

## B.—Tests on Various Irons and Steels Buried at Binfield.

### I.—INTRODUCTION.

The tests on buried specimens of iron and steel to be described in this section were undertaken, with the kind collaboration of the Mid-Wessex Water Company, in the neighbourhood of Binfield, near Wokingham. The main object of the work was to ascertain how far the conditions of exposure affect the experimental results and thus obtain information that would ensure the avoidance of gross errors when it was found possible to proceed with the more extensive experimental programme. The effects of different depths of soil cover, of the orientation of the specimens with regard to the trench and of the proximity of dissimilar metals, *i.e.*, iron and zinc, have been studied. In addition, the opportunity was taken to compare the resistance to corrosion of several different types of irons and steels by burying a representative selection of the materials already exposed by the Corrosion Committee in their atmospheric and marine-corrosion tests, together with two cast irons kindly provided by the Staveley Coal and Iron Co., Ltd. An unambitious attempt was also made to correlate corrosion with soil conditions by burying sets of specimens of three materials only in each of six trenches, dug at sites where examination of the soil had been previously carried out in connection with the laying of a new pipeline. A further examination of soil samples removed from the actual trenches was made at the conclusion of the tests.

### II.—EXPERIMENTAL DETAILS.

#### (a) *Specimens.*

The total number of specimens exposed in the six trenches was 95, of which 86 were iron or steel and 9 zinc. The wrought irons and steels were mostly in the form of "flats" with a standard size of  $15 \times 10 \times \frac{3}{8}$  in. Two cast irons were tested: Vertically-cast iron, represented by curved specimens sawn to the standard dimensions from a 15-in. pipe with an average wall thickness of 0.46 in., and sand-cast cast iron, cast individually to size  $15 \times 10$  in. by about 0.46 in. thick. Zinc specimens in the form of  $\frac{1}{8}$ -in. sheet, 15 in. long by 10 in. wide, were supplied through the kindness of I.C.I. Metals, Ltd. Analyses and other particulars of the various materials are given in Tables I, and II.

TABLE I.—*List of Materials Tested.*

Material.	Number of Specimens.		Average Weight as Received. G.	Average Loss on Pickling. <sup>1</sup> G.
	As-Rolled or Cast.	Pickled.		
<i>Cast Irons.</i>				
CC, vertically-cast . . .	12	...	8587	...
CS, sand-cast . . .	12	...	8016	...
<i>Ingot Iron.</i>				
W . . . . .	2	32	6979	49
<i>Wrought Irons.</i>				
R, Swedish . . . . .	2	2	7260	106
S, Swedish, copper 0.6% . . .	2	2	7279	50
V, Scottish . . . . .	2	2	7220	70
<i>Steels.</i>				
K, chromium 1% . . . . .	2	2	7332	67
M, copper-chromium . . . . .	2	2	6814	52
XK, ordinary . . . . .	2	2	6623	67
ZK, copper 0.5% . . . . .	2	2	6697	44
<i>Zinc.</i>				
Zn . . . . .	9	...	2233	...

<sup>1</sup> The approximate total surface area of a specimen is 2.2 sq. ft. Hence, losses in weight or other data expressed in grammes per specimen may be converted into pounds per square foot of surface by dividing by 1000.

TABLE II.—*Analyses of Materials Tested.*

Material.	Analysis.						
	C. %.	Mn. %.	Si. %.	P. %.	S. %.	Cr. %.	Cu. %.
<i>Cast Irons.</i>							
CC, vertically-cast . . .	3.42 <sup>1</sup>	0.64	2.15	1.24	0.09	...	...
CS, sand-cast . . .	3.22 <sup>2</sup>	0.55	2.00	1.24	0.09	...	...
<i>Ingot Iron.</i>							
W . . . . .	0.03	0.03	0.03	0.01	0.04	...	0.04
<i>Wrought Irons.</i>							
R, Swedish . . . . .	0.03	...	0.02	0.05	0.01	...	Trace
S, Swedish, copper 0.6% . . .	0.02	...	0.02	0.05	0.01	...	0.60
V, Scottish . . . . .	0.03	0.03	0.16	0.17	0.02	...	0.12
<i>Steels.</i>							
K, chromium 1% . . . . .	0.25	0.60	0.12	0.04	0.03	0.98	0.03
M, copper-chromium . . . . .	0.27	0.89	0.15	0.04	0.03	0.60	0.50
XK, ordinary . . . . .	0.21	0.59	0.10	0.04	0.04	0.07	0.03
ZK, copper 0.5% . . . . .	0.23	0.60	0.12	0.03	0.03	0.05	0.50
<i>Zinc.</i>							
Electrolytic . . . . .	Zn > 99.9%						

<sup>1</sup> Graphitic carbon, 2.80%.<sup>2</sup> Graphitic carbon, 2.62%.

*(b) Examination Prior to Exposure.*

All the specimens were weighed, and their strength, breadth and thickness were recorded. Each surface was examined, particular attention being paid to scratches, the removal of rolling scale and any surface imperfections that might subsequently be mistaken for pits. The positions of any such major defects were noted by means of co-ordinates. In the case of the vertically-cast specimens of cast iron, there were numerous vertical grooves on the inner surface together with isolated surface bumps and excrescences.

The zinc specimens had a "polished" bright surface which was almost free from imperfections except for minute longitudinal scratches in the direction of rolling. They were cleaned with carbon tetrachloride before being weighed and examined.

*(c) Pickling.*

As indicated in Table I., in the case of the ingot iron, wrought irons, and steels tests were made both on specimens carrying rolling scale and on specimens that had been descaled by pickling. This pickling was carried out by immersing the specimens in 20% by volume sulphuric acid at 40° C.; 0.05% of di-orthotolylthiourea was added to the bath as an inhibitor.<sup>1</sup> The 46 specimens concerned were reweighed and re-examined after pickling. The losses in weight of the various materials on pickling are shown in Table I. and are normal.

*(d) Exposure Sites.*

The six trenches in which the specimens were exposed were dug at points along the 14-in. main of the Mid-Wessex Water Company running from Beenhams Heath to Wokingham Reservoirs. The trenches were parallel to the pipe, the actual sites being near the positions of test holes, where samples had been taken for analytical and bacteriological analysis shortly before the pipe was laid. The trenches varied in length from 42 ft. to 7 ft. 6 in.; they were about 2 ft. 3 in. wide by 3 ft. 6 in. deep.

The usual procedure was followed when excavating and filling the trenches, with the result that the sub-soil, top soil and turf remained in their normal positions after the specimens had been buried.

Exposure was continued for three years, from September, 1937, to September, 1940.

*(e) Examination of the Specimens after Exposure.*

The iron and steel specimens were dry scratch-brushed to remove as much of the earth as possible. They were then thoroughly

<sup>1</sup> The use of this compound as an acid inhibitor is governed by patents owned or controlled by Imperial Chemical Industries, Ltd., who kindly presented a supply of the material for the present purpose.

scratch-brushed under the cold-water tap, brushed with soap and water and finally sponged with hot water.

The zinc specimens were scrubbed under the tap with an ordinary scrubbing brush, and the preliminary cleaning was completed by scrubbing with soap and hot water, using a nail brush. After drying they were polished with a soft cloth.

The rust adhering to the iron and steel specimens after scratch-brushing was removed by immersing them in the pickling bath already described (sub-section (c) above). In the case of most materials, the inhibitor present prevented any appreciable loss of metal, but when necessary a blank correction was applied for this by enclosing one specimen of each series in a lead hood attached to a gas burette; the rate of hydrogen evolution was measured and the amount of metal dissolved was calculated from this.

The final cleaning of the zinc specimens was carried out as follows: As much as possible of the remaining earth and white corrosion product was removed by careful scratching with a blunt knife, care being taken to avoid removal of any metal. The metal was then rubbed hard with a rag soaked in 10% acetic acid and finally washed in boiling water. It was found that the earth was easily removed, but the corrosion product was very firmly seated at the points of attack. The specimens were treated twice before, on weighing to the nearest gramme, no change in weight was observed.

#### (f) *Final Examination.*

After the specimens had been reweighed, their surface was examined. The exact location of the pits was noted and the five deepest on each face were measured with a spherometer. As a general rule no pit was measured if it was obviously less than 10 mils (0.010 in.) deep.

### III.—DISCUSSION OF RESULTS.

#### (a) *Reproducibility of Results.*

Although, in order to simplify the presentation of the results, average values are given in most of the Tables accompanying this paper, it should be noted that all tests were made on duplicate specimens. The percentage difference in the losses in weight of duplicates has been calculated for the 40 cases in which a direct comparison was possible and the results are summarised in Table III. It will be seen that the average value for half this percentage difference, which corresponds approximately to the probable error of the mean value, is 8.4%. This figure is higher than the values usually observed in field corrosion tests in other media, *e.g.*, the atmosphere and sea-water, probably because of physical heterogeneities in the soil itself, such as the presence of stones and of soil particles of different sizes. It will therefore be advisable in future



tests to expose specimens in triplicate at least, in order to diminish the probable error of the mean results.

TABLE III.—*Reproducibility of Results.*

Difference between Duplicates. <sup>1</sup> %.		Number of Cases.
Range.	Mean.	
0-2	1.4	6
2.5-4.5	3.1	7
5-7	5.8	7
7.5-9.5	8.4	8
10-12	10.0	2
12.5-14.5	13.8	2
15-17	15.8	3
17.5-19.5	18.5	3
20 & upwards	29.0	2
	Mean 8.4	Total 40

<sup>1</sup>  $100(a - m)/m$ , where  $a$  = loss in weight of the more corroded specimen and  $m$  = the mean loss in weight of both specimens.

Without going into detail it may be noted that the difference between duplicate specimens was largely a positional effect, since it was found that in all the trenches a line could be drawn dividing the trench into halves containing the more and the less corroded duplicates, respectively. Positional effects such as these are a natural feature of most field tests on corrosion; they are observed, for instance, in atmospheric exposure, where the corrosion increases with increasing height of exposure above the ground, and in marine immersion tests, where the corrosion decreases with increasing depth of immersion.

#### (b) *Rates of General Corrosion.*

Specimens of ingot iron (*W*), vertically-cast cast iron (*CC*) and sand-cast cast iron (*CS*) were exposed at an average depth of 35 in. to the centre of the specimens (30-in. cover) in each of the six trenches. The cast irons were exposed as received from the foundry, but the ingot iron was first descaled by pickling. The specimens were arranged in two rows running parallel to the sides of the trench; they were placed on one of their long 15-in. sides, so that when buried their surface was vertical. There was approximately 15 in. clearance transversely between the two rows of specimens, leaving about 6 in. from each row to the sides of the trench, whilst there was a gap of 15 in. between the specimens in the longitudinal direction.

The mean losses in weight of the various sets of specimens are  
1942—ii

TABLE IV.—*Losses in Weight and Depth of Pitting of the Three Materials Buried in All Six Trenches. Three Years' Exposure.*

Trench No.	Cast Iron.						Ingot Iron W.		
	Vertically Cast CC.			Sand-Cast CS.					
	Loss in Weight. G.	Pitting. Mils. <sup>1</sup>		Loss in Weight. G.	Pitting. Mils. <sup>1</sup>		Loss in Weight. G.	Pitting. Mils. <sup>1</sup>	
		Maxi-mum.	Aver-age.		Maxi-mum.	Aver-age.		Maxi-mum.	Aver-age.
1	221	38	17	217	46	26	163	14	<10
2	204	37	17	133	41	15	152	32	19
3	254	44	19	217	33	15	256	58	40
4	171	31	17	182	78	31	170	20	12
5	145	29	14	145	58	22	173	52	33
6	172	44	18	150	49	26	211	34	19
Mean	195	37	17	174	51	23	188	35	21

<sup>1</sup> The maximum is the deepest pit on four surfaces. The average is for the twenty deepest pits, five on each surface.

shown in Table IV. It is unnecessary to convert all the data into their equivalents in thousandths of an inch of metal per year, but it may be noted that a loss in weight of 1000 g. per specimen roughly corresponds to the removal of a layer of metal 24 mils (0.024 in.) thick over the whole surface. It will be seen from Table IV. that the average loss in weight of specimens of all three materials was 186 g. in three years, which is equivalent to an annual corrosion rate of 1.5 mils. This figure may be compared with values of 4.3 mils per year observed over five years' exposure to an industrial atmosphere at Sheffield, and to 4.8 mils per year for steel immersed in sea-water at Gosport for fourteen months. It may be concluded that the general rate of corrosion of ordinary ferrous materials in these soils is not unduly severe. Admittedly, the results are isolated determinations and give no indication of the progress of corrosion with time, but in all probability the rate of attack would have slowed down as time proceeded, owing to the consolidation of the soil and of the corrosion products formed. If the rate of general corrosion were assumed to remain constant at 1.5 mils per year, 170 years would be required to corrode through a pipe with a  $\frac{1}{4}$ -in. thick wall. This calculation also assumes, no doubt incorrectly, that the attack is and will remain uniformly distributed over the whole surface, and takes no consideration of pitting, which is discussed later. It may be added that the maximum loss in weight of any one specimen was 275 g. for an ingot-iron specimen buried in trench 3; the minimum was 100 g. for a specimen of sand-cast cast iron in trench 2. Thus, the overall variation in the

rates of corrosion including different materials and all trenches was 2.75 to 1.

(c) *Rates of Pitting.*

Figures for the depth of the maximum pit and the average depth of the five deepest pits are given in Table IV. It will be seen that the deepest pits observed on any one specimen of each material were :

Material.	Mils after 3 Years.
CG, vertically-cast iron . . . . .	44
CS, sand-cast cast iron . . . . .	78
W, ingot iron . . . . .	58

The mean value of these maxima for the three different materials is 60 mils, or 20 mils (0.020 in.) per year. It is interesting to note that this figure is 3 times greater than the mean value for the average depth of the twenty deepest pits.

There is reason to believe, from the previous work conducted in the United States, that the rate of pitting would decrease with time, but if a rate of 20 mils per year were maintained, an unprotected  $\frac{1}{4}$ -in. thick pipe-wall would be perforated in  $12\frac{1}{2}$  years; the life calculated from the average figure for the twenty deepest pits, 6.7 mils per year, would be 3 times greater or approximately 40 years. These figures tally better with practical experience than the life deduced from the average rate of general corrosion.

(d) *Effect of Descaling Specimens before Exposure.*

The effect of the presence of rolling scale on the specimens was studied by exposing duplicate sets of eight different materials in the as-rolled and in the pickled conditions, respectively. The tests were conducted in trench 2, the conditions of exposure being similar to those already described. The results obtained are shown in Table V.

It is evident that the rolling scale has protected the specimens appreciably, since in all cases the loss in weight of the pickled specimens is greater than that of the corresponding as-rolled ones. The observed differences range from 19 to 49 g. per specimen according to the material, but the differences in the weight of metal corroded are greater than this, since the weight of rolling scale on the specimens, some of which would also be removed by the corrosion of the underlying metal, varies approximately from 37 to 55 g. As would be expected, much of the scale remained after exposure on some of the materials; the average amounts ranged from 70% on steel *M* to practically none on ingot iron *W*.

It is known that in marine corrosion the presence of rolling scale on steel tends to promote pitting. It is surprising, therefore, that the protection of the metal by the rolling scale has not been achieved at the expense of an increase in the depth of pitting. On the contrary, it is clear from Table V. that the advantage, if any, in this respect lies with the as-rolled surfaces.

TABLE V.—*Comparison of Different Materials and Effect of Rolling Scale. Trench 2.*

Material.	As-Rolled. <sup>1</sup>			Pickled.		
	Loss in Weight. G.	Pitting. Mils. <sup>2</sup>		Loss in Weight. G.	Pitting. Mils. <sup>2</sup>	
		Maxi- mum.	Aver- age.		Maxi- mum.	Aver- age.
<i>Cast Irons.</i>						
CC, vertically cast . . .	204	37	17	...	...	...
CS, sand-cast . . .	133	41	15	...	...	...
<i>Ingot Iron.</i>						
W . . . . .	112	20	12	152	32	19
<i>Wrought Irons.</i>						
R, Swedish . . . . .	104	26	15	131	32	20
S, Swedish, copper 0.6% . . .	115	23	15	164	34	24
V, Scottish . . . . .	130	30	17	149	21	14
<i>Steels.</i>						
K, chromium 1% . . . . .	143	31	24	162	47	26
M, copper-chromium . . . . .	117	43	29	136	40	30
XK, ordinary . . . . .	113	26	16	149	44	29
ZK, copper 0.5% . . . . .	149	38	23	172	40	26
Mean <sup>3</sup> . . . . .	110	30	19	152	36	24

<sup>1</sup> As-cast in the case of the cast irons.

<sup>2</sup> The maximum is the deepest pit on four surfaces. The average is for the twenty deepest pits, five on each surface.

<sup>3</sup> Omitting the two cast irons.

(e) *Effect of Differences in the Composition of the Materials.*

Considering first the data given in Table IV. for the three materials exposed in all six trenches, it will be seen that over the entire series of tests the losses in weight of vertically-cast cast iron (CC), sand-cast cast iron (CS) and ingot iron (W) were 195, 174 and 188 g., respectively. The maximum difference between any two of them is 21 g., or approximately 11%. Since, as already stated, the average probable error of the results is of the order of 8.4%, it is clear that there is no significant difference between the behaviours of the ingot iron and the vertically-cast cast iron, whilst it is doubtful whether the difference between the sand-cast cast iron and the other two materials has any meaning. In any case, the differences are small for practical purposes and are counter-balanced by the fact that the depths of pitting of the materials (Table IV.) follow the reverse order of the losses in weight.

Further evidence concerning the effects of differences in composition on the resistance to corrosion of wrought iron, ingot iron or steel buried in the soil was obtained from the tests on the effect of rolling scale referred to in the previous sub-section (d). It will be seen from Table V. that the losses in weight of the eight materials



exposed in the pickled condition varied from 131 g. to 172 g. In view of the high probable error of the results, it is doubtful whether the differences between the materials are significant, with the possible exception of those between materials at or near the top and bottom of the apparent order of merit according to loss in weight. It should be noted, too, that this order of merit is entirely different from that observed in atmospheric-corrosion tests, in which, for instance, the Swedish wrought iron *R* is undoubtedly the most corrodible material and the corresponding copper-bearing wrought iron *S* is one of the most resistant. There is some indication from the results shown in Table V. that ingot iron *W* was less pitted than the other materials in tests on specimens exposed with the rolling scale and also that the wrought irons as a class were superior, in this respect, to the steels, but more extensive experimental evidence would be necessary to establish these facts.

It may be concluded that differences in the composition of iron and steel within the range of materials tested are of minor importance in determining the resistance of ferrous materials to general corrosion when buried in the soil. In particular, in contradistinction to atmospheric corrosion, the addition of small amounts of copper to iron and steel has no effect in retarding corrosion under these conditions; this will be seen by comparing the figures given in Table V. for Swedish wrought irons *R* and *S* and for steels *XK* and *ZK*. These pairs of materials are of identical composition, respectively, save for their copper contents. Similar conclusions were deduced by the National Bureau of Standards from the extensive tests carried out by them in the United States.

#### (f) *Graphitisation.*

It was noted after derusting the cast-iron specimens that the vertically-cast specimens had a graphitic appearance and that on drawing the finger across the surface it became covered with graphite. The specimens were further examined by scraping the pits already measured with the point of a penknife and measuring the increase in depth. The surface was also scraped to ascertain whether graphitisation was confined to the pits or was general over the surface. It was found that in seven of the twelve specimens only slight graphitisation had occurred and no significant deepening of the pits was observed after scraping. In the case of the remaining five specimens, original pit depths ranging from less than 10 mils to 44 mils were increased after scraping to from 13 to 70 mils; the maximum increase in the depth of any one pit was 47 mils, namely, from 23 to 70 mils. In general the attack was confined to the pits, and marked graphitisation was found on only one surface of one specimen.

No graphitisation was apparent on any of the sand-cast cast iron specimens (*CS*).

(g) *Effect of the Conditions of Exposure.*(1) *Depth of Burial.*

The effect of the depth of burial was investigated by burying some pickled ingot-iron specimens at four different depths in trench 4, namely at 9, 17, 25 and 33 in., respectively, measured to the centre of the specimens. Two sets were exposed; in one case they were buried with the surfaces horizontal and in the other with the surfaces vertical. In both cases the axis of the specimen was parallel to the sides of the trench. The results of this test are shown in Table VI.

TABLE VI.—*Effects of Depth of Burial and Orientation.*  
*Trench 4.*

Depth of Burial. <sup>1</sup> In.	Vertical Specimens.			Horizontal Specimens.		
	Loss in Weight. G.	Pitting. Mils. <sup>2</sup>		Loss in Weight. G.	Pitting. Mils. <sup>2</sup>	
		Maximum.	Average.		Maximum.	Average.
9	197	53	36	161	42	25
17	197	32	23	159	48	20
25	160	22	16	143	20	12
33	170	20	12	122	16	10
Mean	181	32	22	146	32	17

<sup>1</sup> Measured to the centre of the specimen.

<sup>2</sup> The maximum is the deepest pit on four surfaces. The average is for the twenty deepest pits, five on each surface.

*Vertical Specimens.*—There is no difference in the losses in weight of specimens buried at 9 in. and 17 in. There is a significant drop in loss of weight from 17 in. to 25 in., followed by a rise at 33 in., which is, however, within the experimental error.

*Horizontal Specimens.*—The loss in weight decreases regularly with successive increases in depth, although, as in the case of the vertical specimens, there is very little difference in the losses in weight for the first two depths.

The results indicate that down to a depth of 17 in. there is very little difference in the general corrosion rate, but that below this depth the rate decreases with increasing depth. This decrease is similar to the decrease in the corrosion rate in sea-water with increasing depth of immersion already mentioned. Both phenomena are no doubt due to the same cause, namely, the control of corrosion by oxygen diffusion from above.

*Comparison of Vertical and Horizontal Specimens.*—It is obvious from Table VI. that the loss in weight of the horizontal specimens is less than that of the vertical specimens at each depth; the average difference between the two series is approximately 20%.

There is no systematic difference in the depths of the maximum pits, but the average pitting is greater for vertical specimens than for horizontal ones. In both cases there is a significant decrease in pitting with increasing depth of burial. It should be noted, too, that the under surfaces of the two horizontal specimens at 9 in. depth were appreciably more pitted than the upper surfaces. These specimens were found to have very concentrated pitting with large apparently little-attacked areas on the underside, whereas their upper surfaces were pitted generally to a moderate extent. The slightly attacked areas on the undersides may not have been in good contact with the soil, owing to the local trapping of pockets of air when the specimens were buried.

## (2) *Proximity of Dissimilar Materials.*

In order to test the effect of the proximity of dissimilar materials, three sets of five specimens, each consisting of two specimens of ingot iron sandwiched between three specimens of zinc, were buried in trench 4 at a depth of 31 in. (26-in. cover). The specimens were arranged with their faces vertical, transversely to the trench, and the distance between them was uniform in any one set, being 12 in. in the first set, 6 in. in the second and 3 in. in the third.

TABLE VII.—*Effect of Proximity of Dissimilar Metals.  
Trench 4.*

Material.	Distance between Specimens. <sup>1</sup>					
	3 in.		6 in.		12 in.	
	Loss in Weight. G.	Pitting. Mils. <sup>2</sup> Max.	Loss in Weight. G.	Pitting. Mils. <sup>2</sup> Max.	Loss in Weight. G.	Pitting. Mils. <sup>2</sup> Max.
1. Zinc . . . . .	57	24	59	20	52	16
2. Ingot iron . . . .	125	22	103	10	132	11
3. Zinc . . . . .	52	25	72	18	43	13
4. Ingot iron . . . .	138	11	113	9	105	8
5. Zinc . . . . .	66	22	60	19	65	20
Mean. Zinc . . . . .	58	24	64	19	53	16
Mean. Ingot iron . .	132	17	108	10	119	10

<sup>1</sup> In this Table the data refer to single specimens exposed alternately.

<sup>2</sup> The results did not justify the calculation of average values for the depth of pitting.

On considering the results, which are given in Table VII., four facts present themselves:

(i) The loss in weight of the ingot iron has been reduced by the proximity of the zinc. The mean loss of the ingot iron in the

three sets is 120 g., as compared with 170 g. for vertical specimens buried at 33 in. in the same trench (Table VI.).

(ii) The losses in weight of the specimens bear no relationship to the distance between them. It is, however, interesting to note that in the second set (6-in. spacing), where the ingot-iron specimens have lost least in weight, the zincs have lost the most. The average loss of the zinc is roughly half that of the ingot iron for the three sets.

(iii) The pitting of the ingot iron has been appreciably reduced by the zinc<sup>1</sup> (cf. Tables VI. and VII.). The specimens under discussion showed very little pitting attack after exposure and their surfaces were good.

(iv) The depths of the deepest pits are appreciably greater for zinc than for ingot iron. In both cases there is little difference between the depth of the deepest pit at 12-in. and 6-in. spacing, but at 3-in. spacing there is a substantial increase.

### (3) *Positional Effects.*

The fact that lines of symmetry were found in all the trenches has already been mentioned and need not be discussed further, except for noting that this is an additional argument in favour of exposing at least three specimens of each material.

Observations, which it is unnecessary to record in detail, showed that there was no greater tendency for pitting on an outer face, *i.e.*, one facing the side of the trench, than on an inner one, *i.e.*, one facing inwards; nor, except in the case of the vertically-cast cast iron, was there any difference in the behaviour of different faces of the same material.<sup>2</sup> In the case of the vertically-cast cast iron the inner surface of the pipe was more pitted in 10 cases out of 12; it will be recalled that this surface was found to be grooved and rough on examination before exposure.

One further remark may be made in this sub-section. Several of the experimental trenches were in the neighbourhood of trees and ditches, and it was evident at the conclusion of the tests that it will be desirable to avoid this in future experiments. Both these factors lead to good drainage of the experimental trench, so that the results obtained tend to be typical of the site itself rather than truly representative of the soil in which the tests are conducted.

### (4) *Effect of Different Soil Conditions.*

As already stated, samples of soil were taken for examination from all six experimental trenches. The results have been compared with the values observed for the corrosion of the specimens

<sup>1</sup> Pits less than 10 mils in depth were measured on these specimens.

<sup>2</sup> Since one face of a hot-rolled flat or plate is in contact with the mill floor and slides or rolls along it, whilst the other is freely exposed to the atmosphere, the properties of the rolling scale may differ on the two faces.



in the different trenches, but no correlation has been found between the corrosion and any of the soil characteristics examined. It is probable that this lack of correlation is due to the fact that all the soils were essentially of the same type and that the relatively small differences in the average corrosion rates in the various trenches are also due to this cause. It may be noted that, after conducting tests on specimens buried in 47 soils, deliberately selected as having widely different characteristics, the U.S. National Bureau of Standards were unable to reach definite conclusions as to what soil characteristics determined the corrosion of buried metals. It is clear that, to explore the matter further in Great Britain, it will be necessary to expose specimens in a wider variety of soils.

TABLE VIII.—*Summary of the Results of Examinations of Soil Samples.*

	Max.	Min.
<i>Chemical Analysis, 1937.</i>		
SiO <sub>2</sub> . % . . . . .	77	61
Fe <sub>2</sub> O <sub>3</sub> . % . . . . .	13	7
Al <sub>2</sub> O <sub>3</sub> . % . . . . .	19	6
CaO. % . . . . .	2.7	0.8
MgO. % . . . . .	2.0	0.4
CO <sub>2</sub> . % . . . . .	0.94	0.04
SO <sub>3</sub> . % . . . . .	0.09	Trace
SO <sub>3</sub> , soluble. % . . . . .	0.07	Trace
NaCl, soluble. % . . . . .	0.29	0.06
pH . . . . .	8.5	5.0
<i>Chemical Analysis, 1940.</i>		
Water-soluble CaO. P.p.m. . . . .	410	50
Water-soluble SO <sub>4</sub> . P.p.m. . . . .	460	40
Saturation capacity <sup>1</sup> . . . . .	19.8	7.8
<i>Mechanical Analysis, 1940.</i>		
Stones 2 mm. <sup>2</sup> % . . . . .	51.8	0.5
Coarse sand. <sup>2</sup> % . . . . .	53.5	4.6
Fine sand. <sup>3</sup> % . . . . .	41.4	21.7
Silt. <sup>3</sup> % . . . . .	21.3	4.3
Clay. <sup>3</sup> % . . . . .	39.5	11.7

<sup>1</sup> Milligramme equivalents of base per 100 g. of soil; if the base were all calcium, 1 milligramme equivalent would equal 20 mg. of calcium.

<sup>2</sup> As percentage of total air-dry soil.

<sup>3</sup> As percentage of oven-dry fine earth.

Under these circumstances, there would be little point in giving full details of the results of the examination of the soils. Representative figures, which suffice to characterise the type of soil in which the tests were made, are given in Table VIII. It should be noted that no detailed examination of the soils was carried out at the time of exposure, because it was thought preferable to make the examination at the time of removal, when the soil had settled down again. The results in Table VIII. dated 1940 were obtained

at Rothamsted on samples taken at the conclusion of the tests; the analyses dated 1937 were made by the Staveley Coal and Iron Co., Ltd., when the pipe-line was being surveyed, and refer to samples taken from test holes near which the trenches were subsequently dug.

Samples were taken for bacteriological examination from each trench, in each of the following positions: (a) Top soil, (b) soil 6 in. from the specimens, (c) soil in contact with the specimens. In all cases, except the top soil in trench 1, appreciable numbers of sulphate-reducing bacteria were present in 1-g. samples of the soils; in fact, with one additional exception, organisms were detected in 0.1-g. samples. These results do not necessarily show that sulphate-reducing bacteria were responsible for the corrosion, but rather that, given satisfactory conditions, they could have played a part in the process. In most cases it seemed clear that the bacteria had had no effect, but an attempt was made to confirm this by determining the amount of sulphide present in the soil samples. This was inconclusive, but it will be desirable in future work to extend, in appropriate cases, these attempts to correlate corrosion with the sulphate-reducing bacteria present in the soil by comparing the sulphide content of the bulk of the soil with that of the soil immediately adjacent to the specimens and that of the corrosion product itself. Such analyses will be particularly desirable in the case of specimens buried in clay soils, where the conditions are suitable for the activity of the organisms.

### C.—Electrical Resistance Tests.

#### I.—PRINCIPLE OF THE ELECTRICAL-RESISTANCE METHOD.

A method in which the change in the electrical resistance of metallic specimens was used to determine their corrosion was developed by one of the authors in 1929<sup>1</sup> and was successfully applied to a study of the atmospheric corrosion of non-ferrous metals. The method depends on the fact that the surface of the specimen is converted by corrosion into corrosion products which are either removed by rain or, if left in position, are extremely poor electrical conductors as compared with the original metal. If the cross-section of the specimen is sufficiently small, the effect of corrosion on its electrical resistance is appreciable and may be easily detected with simple apparatus.

It seemed possible that the method would also be of value in the case of buried metals. It should be practicable, by taking leads to a point above ground from the ends of a buried specimen of suitable design, to follow its corrosion by periodic measurements of its electrical resistance, whilst leaving it undisturbed. This procedure would have the great advantages of enabling corrosion/time curves to be determined for the same specimens and of reducing

<sup>1</sup> J. C. Hudson, *Transactions of the Faraday Society*, 1929, vol. 25, p. 177.

the considerable labour involved in preparing, burying, excavating and examining the numerous sets of similar specimens that have to be exposed in order to make successive determinations by the loss-in-weight method. On the debit side it must be recognised that electrical resistance measurements are most conveniently made on specimens of small cross-section, such as coils of wire of, say,  $\frac{1}{8}$  in. dia., the behaviour of which may bear no quantitative relationship to the corrosion of massive specimens such as 6-in. pipes; moreover, they would yield no information concerning the rate of pitting, which is often of paramount importance. Despite these limitations, the electrical-resistance method should prove a useful supplement to the more usual loss-in-weight and pit-depth tests on massive specimens; for instance, it might prove a convenient means of assessing the relative corrosiveness of different types of soils.

The corrosion of metals buried in the soil differs from that of metals exposed in the open atmosphere, inasmuch as the specimens are surrounded by a solid medium and that most of the corrosion products form a cake on the surface of the metal. In order to demonstrate that the electrical-resistance method can also be successfully applied to buried metals it is therefore necessary to show:

(a) That electrical-resistance measurements can be conveniently carried out on buried specimens and that the corrosion products formed and the surrounding soil itself do not interfere seriously with the accuracy of the measurements.

(b) That the changes in electrical resistance bear a direct proportion to the amount of corrosion as determined by loss-in-weight determinations.

The experimental work described in this section was undertaken with the above objects in view. Since corrosion, even in the most aggressive soils, is comparatively slow, the experimental method adopted consisted in burying a helix of mild-steel wire in the soil and corroding this artificially by electrolysis. From time to time the electrolysis was discontinued for a few moments while the resistance of the helix was being determined. The number of ampere-hours used for the electrolysis was determined at each stage, and at the end of the experiment the theoretical loss in weight was calculated from the total by Faraday's law. This value was compared with the observed loss in weight of the helix so as to give a figure for the efficiency of the electrolysis, which was found to range from 74 to 95%. It can be shown that the theoretical relationship between the resistance of the helix,  $R$ , and the number of ampere-hours,  $Y$ , is

$$R = W_0 R_0 / (W_0 - eFY)$$

where

$R_0$  is the initial resistance of the specimen,

$W_0$  is its initial weight,

$e$  is the efficiency of electrolysis,

and

$F$  is the appropriate electrochemical factor.

Further details of the experiments are given later, but a glance at the experimental results shown graphically in Fig. 1<sup>1</sup> makes it

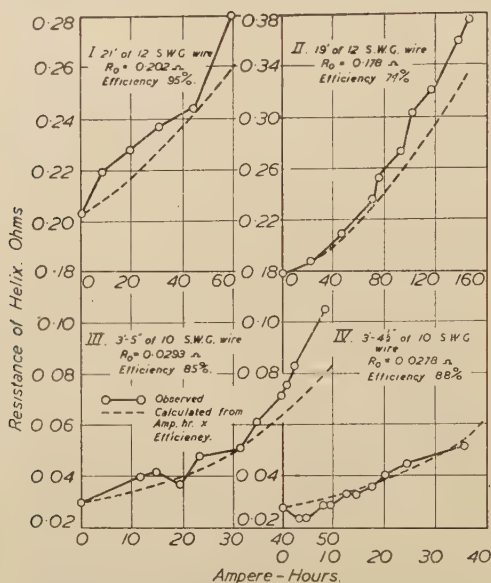


FIG. 1.—Change in the Resistance of a Buried Steel Helix due to Corrosion.

clear that the essential purpose of the experiments has been achieved. It can be concluded that it is possible to follow the change in the electrical resistance of specimens buried in the soil and that this change is a reasonably good indication of the extent to which they have corroded.

## II.—EXPERIMENTAL DETAILS.

Four experiments were made in all, but it is unnecessary to describe each one at great length. The most important feature is the design of the specimens themselves, which will be clear from Fig. 2. The resistance specimen consisted of a helix of bright steel wire.<sup>2</sup> In the first two experiments about 20 ft. of 12-S.W.G. (0.104-in. dia.) wire were used with a total resistance of about 0.19 ohm; in the last two experiments the total resistance was reduced to about 0.028 ohm by using about 3 ft. 6 in. of 10-S.W.G. (0.128-in. dia.) wire. The helix had an internal diameter of

<sup>1</sup> The dotted lines in this diagram are curves calculated from the theoretical relationship given above.

<sup>2</sup> Of the solid silicon type (carbon 0.11%, silicon 0.09%), kindly supplied by Dr. T. Swinden.



approximately 3 in. It was made the anode in the electrolysis circuit. The cathode consisted of a piece of iron tube, 2 in. in dia., placed inside the helix in the form of a core. Its ends were held in two wooden supports, as shown in Fig. 2, and it was separated from the helix by two wooden distance pieces. The depth of burial was 8 in., measured from soil level to the axis of the helix.

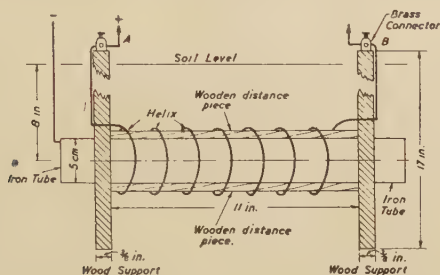


FIG. 2.—Specimen used for the Resistance Tests.

Of the methods used for the electrolysis of the helix and for determining its resistance, it will suffice to say that the circuits were devised to make use of such simple apparatus as was already available in the laboratory. Consequently the experimental accuracy, although sufficient for the purpose in view, was not great and was of the order of 1%. The sensitivity of the resistance circuit has an important bearing on the dimensions of the specimen, the ideal being to use the most massive specimen for which a significant change in resistance can be detected within the desired time. It is probable that by using more sensitive apparatus the diameter of the wire used for the helix could be substantially increased.

In experiment I. the electrolysis current varied from 0.25 to 0.60 amp., in experiment II. from 0.90 to 1.00 amp., in experiment III. from 0.24 to 0.50 amp. and in experiment IV. from 0.17 to 0.41 amp. With the exception of experiment II., which lasted for 150 hr., electrolysis was continued for 120 hr.

#### D.—Proposals for Further Work.

The experimental work described in the last section shows that the electrical-resistance method of determining corrosion in the soil is applicable to cases in which corrosion is artificially produced by electrolysis. The next step is to demonstrate that the method can also be used for measuring the much slower rates of corrosion resulting from burial under natural conditions. There is no doubt that it would be sufficiently sensitive, since, assuming the annual corrosion rate of 0.0015 in. deduced from the loss-in-

weight tests at Binfield it can be calculated that the annual increase in the resistance of steel wires buried for one year under similar conditions should be as follows :

Gauge. S.W.G.	Diameter. In.	Increase in Resistance. %.
10	0.128	4.9
12	0.104	6.0
14	0.080	7.9
16	0.064	10.1
18	0.048	13.8

It will be necessary to correlate the results of the electrical-resistance tests on wires with those of loss-in-weight tests on pieces of pipe or on flat specimens of the same materials. To do this it will be desirable to bury sets of specimens of each type in several different soils. The electrical-resistance measurements could be made at intervals of three or six months, but it would be necessary to wait until the completion of exposure to obtain the correlation with the loss-in-weight determinations. If it should then be found that the order of corrosiveness of the soils was the same whether determined by electrical-resistance tests or by the loss-in-weight method, a considerable advance would have been made.

Some work will be necessary to determine the best shape and dimensions of the specimens for electrical-resistance tests.

Concurrently with the experiments suggested above, a comparison should be made of the behaviour of solid flat specimens and of sections cut from pipes of the same material. It would obviously be an advantage if tests on flat specimens could be accepted as indicative of the behaviour of pipes, but it would be dangerous to assume that this will prove to be so. Consequently, it will be advisable to conduct tests on various methods of sealing the ends of pipe specimens to prevent corrosion of the inner surface during burial.

In view of the abnormal conditions in wartime, it will be desirable to limit the scale of the proposed work as much as is consistent with the achievement of the desired objects, and in particular to limit the number of experimental sites. The ideal would be to find a number of sites with widely different characteristics in the Birmingham neighbourhood and as near together as possible, so that they could all be visited on the same day.

*CORRESPONDENCE.*

Mr. J. WHITCHER (Messrs. Kennedy and Donkin, London) wrote : The results of tests on the corrosion of cast iron are of great practical and economic interest, because of the bearing that they may have on the presumed life of water supply mains. If it could be established that particular types of cast iron used in pipes have more or less susceptibility to corrosion of a dangerous character, that should greatly influence practice in this wide field. In the paper results are given for two types of cast iron, one cut from vertically cast pipes and the other sand-cast to size. It may be that these specimens, although supplied by the Staveley Company, cannot be taken as representative of the materials used in pipe-casting practice; but they exhibited some distinctive characteristics and possibly the makers expected differences, although the compositions were very similar.

Some experiences that I have had with the corrosion of water mains justifies my expression of a wish that some greater attention had been given to the classes of pipe iron which were subjected to test. For instance, there is now a strong practical distinction between sand-cast pipes and spun-cast pipes, and the latter are completely ousting the former except in respect of fittings. It is disconcerting on that account to encounter experience which seems to prove incontestably that the older and superseded sand-cast pipes are much more immune from corrosion of the dangerous pitting type. Since the thickness of spun-cast pipes may be 25% less than that of sand-cast ones, such influence on the ultimate life of the installation may be quite serious.

From the comparisons given in Table IV. it can be seen that the vertically-cast pipe metal exhibited 11% greater loss and 26% less average pitting than the sand-cast specimens; also that the former showed graphitisation at the bottom of the pits, whereas it was not apparent at all on the latter. This seems to indicate that the graphite may be a protection against the deepening of the pits, but not against the widening of them. That it should be protective on balance would be contrary to my observations, which give me reason to believe that this graphite, when it remains in contact with the metal, greatly accelerates the deepening of the pit, owing to local electro-chemical action. This graphitisation at the bottom of deep pits is very pronounced in many instances of corrosion of pipes in the ground. How much of it is graphite and how much black oxide of iron should be accurately determined.

The authors do not give much attention to electrolytic corrosion, but it cannot be ignored in any practical problem of corrosive damage, when the metal is surrounded with material that can become an electrolyte. I think it is generally accepted that all corrosion is electrolytic in character, being an electro-chemical action taking place within small spaces. The range of this action

is restricted either by the small areas of the metal surfaces which become the cathodes and anodes or by the small bulk of the electrolyte concerned at each individual point of activity. The magnitude of the action is restricted by the same causes.

Now, it is clear that the range of any one of these activities can be considerably extended if the masses and surfaces of the metal and of the electrolyte are sufficiently extensive. The electric currents which are the result of the electro-chemical action at the anode (or corrosion) surface can travel very easily in the metal without significant loss of voltage from the many distant points on the surfaces where the contact with the electrolyte is favourable for cathodic reaction. The ionic chains formed at these multiple cathodes in the electrolyte complete many separate circuits from the anode ; and they pick up free oxygen from the soil to carry on and concentrate the activity without the need for subtracting any of the corrosive energy from the circuits to dissociate this oxygen from its compounds.

This is long-range electrolysis, and it is easy to realise how it can activate and make continuous the concentrated and pitting corrosion which is so often observed on iron pipe systems laid in the ground. The electric currents originated in this way can be found travelling many yards through sections of water mains, and they are always evidence that corrosion is active at various points on the surfaces of such mains. It is, by the way, much too easy to say that these currents have been introduced from outside. In some cases they may be, and they cause corrosion in the same way, but it is better not to be misled into vain and difficult search after the source.

The metal jointing of water mains provides the low electrical resistance required even for the small currents concerned, and it is obvious that the new rubber jointing which has been favourably received will have a beneficial influence on the corrosion trouble, as it will tend to restrict the long-range electrolysis within the 9-ft. or 12-ft. lengths. Steel or wrought-iron pipes are defenceless in this respect, and this may help to explain the rapidity of the corrosion experienced with them.

The condition of the protective coating on cast-iron pipes has a considerable influence on the initiation of pitting corrosion. Frequently there can be found a line of pits along the top of a main as though the coating had been damaged by hobnails. This is most likely to have occurred on pipes laid in wet trenches before the era of gum boots. The clean metal surfaces under the damaged spots are very apt to become anodic, whereas the surfaces under the sound compound, as it slowly deteriorates and becomes absorbent, appear in the course of years to become strongly cathodic, so that pits are seldom found on them.

There are also cases of sections of a main being laid in wet "aggressive" ground connected up to sections lying in better conditions. These are very liable to long-range electrolysis.



I trust that the above will not be taken as criticism of a very useful research directed to a particular purpose. I want rather to suggest further research on points in the corrosion problem which may prove of great practical importance.

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### AUTHORS' REPLY.

The AUTHORS, in reply, wrote: We thank Mr. Whitcher for his constructive comments. We agree with him as to the desirability of obtaining information on the corrosion-resistance of different types of cast-iron pipe that could be applied to practical problems, but should make it clear that such comparison was outside the scope of this preliminary research and was not in fact contemplated by us. The two samples of cast iron tested by us were intended to represent cast iron as distinct from steel rather than to be typical of any particular type of pipe; consequently, too much importance should not be attached to any apparent difference between them. Actually, the cast-iron specimens *CC* were cut from a 15-in. pipe cast vertically in a sand mould and not from a centrifugally-cast pipe, as Mr. Whitcher seems to assume. The initials "*CC*" may have misled him; they were originally intended to stand for "centrifugally cast," but in the end these specimens had to be cut from a vertically-cast pipe as stated, because no suitable centrifugally-cast pipe was available at the time. As to the sand-cast iron specimens, *CS*, these were cast singly to size 15 in.  $\times$  10 in.  $\times$   $\frac{1}{2}$  in. in green-sand moulds, so that they may not have been fully comparable with specimens cut from an actual pipe.

In general, we doubt whether a true comparison of different classes of pipe, *e.g.*, sand-cast and spun-cast, could be made on the basis of tests on comparatively small pieces cut from them, and consider that the best method of assessment would be a direct comparison of full-length pipes of the different types in use in the same pipe-lines. Statistical analysis might be required to determine the results. We hope to explore the possibility of tests of this type in collaboration with the pipe manufacturers.

We recognise the importance of electrolytic corrosion. It is difficult to introduce this factor into a small-scale test and we think that Mr. Whitcher will agree that in preliminary work, such as this, it is desirable to avoid the introduction of complicating factors. Probably this problem, too, would also be best attacked on a practical scale using full-sized pipes as specimens.

Mr. Whitcher's association of pitting along the top of a main with damage to the coating by hobnails has an interesting parallel in the case of steel railway sleepers. Here it is a fact that the initiation of corrosion on the sleeper plates is caused by damage to the coating from the hobnailed boots of gangers walking up and down the line.



# THE FIRST CAST-IRON CANNON MADE IN ENGLAND.<sup>1</sup>

By H. SCHUBERT, M.A., D.PHIL. (READING UNIVERSITY).

## SUMMARY.

The iron-casting process was introduced into England at the end of the fifteenth century by French founders, mostly belonging to the King's artillery as gunners in the Tower of London. As a result several ironworks were set up around Ashdown Forest in Sussex before 1500. In one of them, at Newbridge, guns were made with a barrel of cast iron and detachable chambers (mentioned in accounts of 1509-10 preserved in the Public Record Office in London). These are the first cast-iron cannon of English manufacture which can be definitely dated and located. That is thirty-four years before 1543, which, according to historical tradition, is the date of the first casting of iron guns in England known to us. Round about 1509 there was already a considerable home industry in iron in South England, many of the Frenchmen who introduced the casting process being replaced by English founders. This growing home industry was seriously hampered when Henry VIII. engaged French and Italian metal-founders to cast ordnance of bronze and imported guns from Belgium. A new impetus came in 1543, when Henry VIII. was in need of large quantities of ordnance of cast iron, which was less expensive than bronze. This need led to the revival of the casting of iron guns, first at Buxted, where the French bronze-founder Peter Baude and the English iron-founder Ralph Hogge cast iron guns in the same year. From this attempt dates the great development of the casting of iron ordnance in Sussex, and later in South Wales also. At that time the quality of English iron guns was improved by casting the barrel and chamber in one whole piece. The improved quality led to an increasing export to the Continent. The English guns of cast iron held a very high position in the European market well into the seventeenth century, when the demand was limited by Swedish and Westphalian competition. For casting heavy iron cannon of large size double furnaces, *i.e.*, a pair of furnaces combined in a single structure, were erected, the first in Worth Forest in Sussex, in 1547. Afterwards the idea of the double furnace was probably introduced from England into France and into the Netherlands, whence it was carried to Sweden and Western Germany.

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THE age of the Tudor Kings (1490-1603) is a landmark in the growth of the English Nation. Economically this age was marked by the first successful striving for commercial and industrial independency.

The development of the English iron industry during this era was very remarkable; it was mainly due to a twofold impulse, the increased demand for household articles of iron and for armaments. In satisfying both these demands valuable help was afforded by one of the great revolutionising inventions of the earlier times, the casting of iron, which was introduced into England during

<sup>1</sup> Received August 17, 1942.

the early years of the Tudors. It was particularly for armaments that iron-founding proved to be very valuable. Cannon of cast iron could be produced much more cheaply than those of bronze or wrought iron, which were commonly used up to that time.

According to the historical tradition beginning with Raphael Holinshed's *Chronicles* of 1586, the first founding of iron cannon in England took place at Buxted, in Sussex, in 1543.

There are records of iron cannon made in England during the fifteenth century, but the kind of iron used in their manufacture is not mentioned.<sup>2</sup> Two early specimens of mortars were also found in Sussex, the Bodiam Castle mortar, now at Woolwich, and the Eridge gun. They are of wrought iron, with parts of cast iron. Both these mortars are neither dated nor are their places of origin really known; they are named after the places where they were found. The Bodiam mortar is "more likely of foreign origin."<sup>3</sup>

The date 1543 appears to be rather late for the beginning of the casting of iron guns in England, as the method of founding iron was known in Sussex as early as 1490, when there were "iron-founders" working at Buxted, south of Ashdown Forest.<sup>4</sup> A few years later there was an iron-founder, named Pieter Roberdes, at the King's iron mill at Hartfield, north of Ashdown Forest; his second name "Graunt Pierre" indicated his French origin.<sup>5</sup>

Iron-founding increased in 1496, when King Henry VII., preparing to secure the border against a Scottish invasion, gave orders to engage artificers, "founders" and labourers for the building of foundries for the making of iron ordnance. As a result of this commission large quantities of cast-iron "gun-shot" for the King's artillery were made in Ashdown Forest from December, 1496, onwards. One of the founders was Pieter Roberdes, at Hartfield, mentioned above. Another was Simon Ballard, at Newbridge, in Ashdown Forest. For casting he used "rough iron" delivered to him from the King's iron and from iron belonging to Henry Fyner. A third of these founders was Blasius Ballard, perhaps a brother of Simon. All three were at the same time in the service of King Henry VII. as gunners of the Tower of London.<sup>6</sup>

The gunners of that age were not only artillerymen but also experts in shot- and gun-founding. When Henry VII. became

<sup>2</sup> L. F. Salzman, "English Industries of the Middle Ages," pp. 161-163. Oxford, 1923: Clarendon Press.

<sup>3</sup> E. Straker, "Wealden Iron," pp. 145, 257-259 (illustration of Bodiam Castle mortar). London, 1931: G. Bell & Sons, Ltd.

<sup>4</sup> Lambeth Palace, Court Roll, 1352.

<sup>5</sup> Public Record Office, Early Chancery Proceedings, Bundle 222, No. 12. Straker, *loc. cit.*, p. 246.

<sup>6</sup> Calendar of the Patent Rolls, Henry VII., vol. II., p. 92. London, 1916: H.M. Stationery Office. Blasius and Simon Ballard (or Byllard) were appointed gunners on May 15, 1495, *see* Calendar of the Patent Rolls, Henry VII., vol. II., p. 15.



King, in 1485, he kept in his service as gunners William Nele and Patrick de la Mote, appointed by his predecessor, King Richard III.<sup>7</sup> The more important of them was de la Mote, as he was given the office of chief "canoner" or master founder and surveyor and maker of all the King's cannon in the Tower of London and elsewhere. To attend him in the making of cannon two more gunners were appointed, Theobald Ferrount and Gland Pyroo, but there is no information as to which cannon they made nor what kind of material they used. Judging from their names, these three gun-founders were obviously French.

The predominance of French gun-founders and gunners is easily understood if one considers the fame which the French artillery had gained at that time. It dated from the reconquest of Normandy in 1449-50 by the perfected siege artillery of the brothers Bureau. Later those cannon aroused the admiration of the Italians during Charles VIII.'s expedition into Italy in 1494; Guicciardini, the Florentine historian, was deeply impressed by their splendid quality, the rapidity of firing and the use of iron balls instead of stone ones.<sup>8</sup>

One of the merits of King Henry VII. was his full understanding of the importance of artillery. This great monarch consequently enlarged the body of his gunners more and more. In 1489 they numbered 30; in 1497 there were 49 gunners at the Tower. Many of them were of foreign origin, from the Low Countries (Antwerp, Guylder, Harlem) and from Spain, while most of the foreign gunners had French names like Grand Pierre and Ballard (or Byllard).<sup>9</sup>

It is remarkable that those founders who made shot of cast iron in Ashdown Forest were gunners of French origin. That leads to the conclusion that the new method of casting iron was introduced into England from France; this is supported by the terms "founder," "finery," "chafery," which occur in the same or similar form in French.<sup>10</sup>

As a result of the introduction of the iron-founding process several ironworks were installed before 1500, all around Ashdown Forest, where large resources of wood, especially of oak, provided the necessary supply of charcoal for the smelting process. There were the foundries of Buxted in the South and of Newbridge and

<sup>7</sup> Calendar of the Patent Rolls, Edward IV., Edward V., Richard III., pp. 405, 448, 483. London, 1901: H.M. Stationery Office. Calendar of the Patent Rolls, Henry VII., vol. I., p. 48. London, 1914: H.M. Stationery Office.

<sup>8</sup> F. Guicciardini, "Storia d'Italia," A. 1494, lib. I., fol. 25 (edit. 1580). C. Oman, "A History of the Art of War in the Middle Ages," vol. II., p. 226. London, 1924: Methuen & Co., Ltd.

<sup>9</sup> W. Campbell, "Materials for a History of the Reign of Henry VII.," vol. II., p. 437. London, 1877: Longman & Co. Public Record Office. Miscellaneous Books No. 8, pp. 131-132, 158-159.

<sup>10</sup> Rhys Jenkins, "The Beginnings of Ironfounding in England," Collected Papers, p. 119. Cambridge, 1936: University Press.

Hartfield in the North. Near the foundry at Hartfield there was an iron forge, also worked by a Frenchman called John Stile, who had been in England since 1491.<sup>11</sup>

The products of these foundries, so far as they were of cast iron, were gun-shot, but we do not hear of any guns at all. The guns of that time were still mostly made of non-ferrous metal or of wrought iron. It took some time for these early founders to become skilful enough to try their art on so big and difficult an object as a gun. The first attempt was made in 1508; it took place at the foundry where the first cast-iron shot had been made, at the King's iron mill near Newbridge in Ashdown Forest. The founder was again a Frenchman, called Pauncelett Symart, who had been the tenant of the iron mill since 1498.

In the accounts of 1508-09 iron guns with powder-chambers made by Symart are mentioned for the first time, but these guns were no good, as they burst when being tested. Symart was temporarily imprisoned in the Fleet in London together with one Henry Crymer or Craymer (obviously an English name), who was one of the gunners of the Tower, probably the instigator of this gun-founding and Symart's adviser from the ordnance point of view. During the following year Symart cast other guns, with better results; according to the accounts of 1509-10 he made "III. caste gonnes of irron with VII. chamberys of yrron."<sup>12</sup>

This is the first time of which we know definitely that guns of cast iron were successfully manufactured in England.

The weight of the three guns was 2142 lb., that of the seven chambers 2975 lb. That makes an average weight of 714 lb. for the gun or barrel and of 425 lb. for the chamber. The weight of 1139 lb. for the whole gun including the chamber corresponds with that of the smaller type of Tudor ordnance.<sup>13</sup>

As guns and powder-chambers are mentioned separately, the chambers were probably detachable. Of the guns only is it said that they were of cast iron, not of the chambers. Evidently the new process of casting iron was applied to the manufacture of the barrel only. The chambers were probably composed of wrought-iron bars bound together by iron bands, which was the older method of making iron guns.

Pauncelett Symart worked at the foundry near Newbridge until St. Michael's Day in 1511. He was succeeded by Humphrey Walcot, who operated the foundry until his death in 1515. It

<sup>11</sup> W. Page, "Letters of Denization and Acts of Naturalisation for Aliens in England," Publications of the Huguenot Society of London, vol. VIII., p. 225. London, 1887. Straker, *loc. cit.*, p. 245.

<sup>12</sup> Public Record Office, Receiver's Accounts of the Possessions of the Duchy of Lancaster in Sussex, Bundle 454, Nos. 7329-7331. One, "Lamber Symar," born in Normandy, had been an "ironmaster" in England since 1494, *see* Page, *loc. cit.*, p. 228.

<sup>13</sup> *See* list in Laird Clowes, "The Royal Navy," vol. I., p. 404. London, 1897: Sampson, Low & Co. Quoted by Straker, *loc. cit.*, p. 159.

was untenanted until 1524, when it was let to Thomas Boleyn, later Earl of Wiltshire, the father of Anne Boleyn.<sup>14</sup>

The casting of iron guns and shot in Ashdown Forest did not cease after the first attempts. In 1513 Reignold Robertes, perhaps a son of Pieter Roberdes at Hartfield, made two guns of cast iron weighing 1862 lb. for King Henry VIII. After 1511 we find Robert Scorer, at Parrock, also a gunner of the Tower, casting iron shot for the Royal Navy. At the same time Richard Sackfield and John Bowyer, in 1514, at Hartfield, were supplying iron gunstones. In 1509 Claudius Robynson erected a steel forge, also useful for armament purposes, quite near to Newbridge foundry.<sup>15</sup>

This shows that ironmaking was still going on in Ashdown Forest at the beginning of Henry VIII.'s reign, but there is one noticeable difference from earlier times. The French founders were now mostly replaced by Englishmen, who had learnt the process of iron-casting from them.

Unfortunately this growing home industry was soon cut short by the line that the armament industry took afterwards. The turning-point was the great expansion of the Navy which took place under the auspices of Henry VIII., who was keenly interested in it. Concerning the Navy, Henry VIII. followed in his father's footsteps, as Henry VII. was the first English monarch to build vessels specially for war, instead of relying entirely upon ships hired from the merchants. For the armament Henry VII. had created a home industry with the help of French founders and gunners. His son, Henry VIII., acted differently by placing large orders for armaments in foreign countries, especially the Low Countries, which were under the rule of Maximilian of Austria, for whom Henry VIII. had a great personal admiration, based upon a common interest in all kinds of armour. At Mechlin, at that time one of the principal foundries in Europe, the great Flemish gun-founder Hans Poppenruyter (*obit* 1534) made large numbers of guns for the English King. On the other hand, Henry induced alien gun-founders to settle in London. In this way two new foundries were created. One was at Salisbury Place, where Italian gun-founders of the noted family Arcanus of Cesena worked until 1545. The other one was at Houndsditch; it had been in existence since 1511, but was enlarged by Peter Baude, a Frenchman, working there from 1528 to 1546. Until 1571 it was one of the principal gun foundries in England.<sup>16</sup>

<sup>14</sup> Public Record Office, Receiver's Accounts of the Possessions of the Duchy of Lancaster in Sussex, Bundle 454, Nos. 7332, 7333. Margaret Richards, "The Wealden Iron Industry," p. 66. London, 1921 (in typescript only).

<sup>15</sup> Letters and Papers, Henry VIII., vol. I., No. 1463; vol. I., 2nd edition, No. 3613; vol. II., Nos. 1450, 1452, 1454. Straker, *loc. cit.*, pp. 242, 245. Public Record Office, Receiver's Accounts of the Possessions of the Duchy of Lancaster in Sussex, Bundle 454, No. 7331.

<sup>16</sup> C. Ffoulkes, "The Gun Founders of England," pp. 4, 43-44, 47, 106, 117, 123, 133. Cambridge, 1937: University Press.

The greater part of the cannon cast abroad and all those cast in the London foundries were made of non-ferrous metal. The cost of that material was much higher than that of iron. At the beginning of his reign Henry VIII. was well able to meet such expenses, thanks to the treasure that his father had carefully collected, but in the later years the financial resources of this splendour-loving King became completely exhausted, so that when in 1543 war with France became imminent and armaments had to be increased, there was a need for guns of iron because of their lower cost. Unfortunately, since 1510 the making of iron guns for ordnance had been in the hands of the Kings' master smith, Cornelius Johnson, an alien from the Dominions of the German Emperor, probably from the Low Countries, but only guns of wrought iron were made under his supervision, a rather elaborate operation and therefore expensive too.<sup>17</sup>

It was very fortunate for the King and his country in such precarious times that iron-founding was still going on in Ashdown Forest. Up to 1543 iron gun-shot were cast under the supervision of William Levet, Parson of Buxted, but no guns.<sup>18</sup> Levet held the post of the King's "maker of iron stones for the Office of the Ordnance in the Tower," which post passed after his death to Ralph Hogge, his servant and helper in iron-founding.<sup>19</sup>

From the list of aliens made "denizens" in 1544, we know that many ironworkers of French origin were still employed in the ironworks around Ashdown Forest. Most of them came from Picardy and Normandy; they had been in England for many years, some since 1508 and 1509. The works employing the highest percentages of Frenchmen among their ironworkers were those of Levet, mentioned above, who had ironworks at Oldlands, north-west of Buxted, and the ironworks of Thomas Seymour, Duke of Norfolk, at Sheffield, in the parish of Fletching.

As, in 1543, Levet was the only one supplying the Office of the Ordnance with munitions of cast iron, his works was the most suitable place for casting iron guns when King Henry VIII. needed large quantities of ordnance, which could be manufactured more cheaply from cast iron than from bronze or wrought iron. So Henry sent his metal-founder Peter Baude to Buxted, where he cast iron guns in 1543 along with Levet's iron-founder Ralph Hogge. This event lives in English history as the first attempt of such a kind, but we have no contemporary record disclosing

<sup>17</sup> Letters and Papers, Henry VIII., vol. I., Nos. 495, 1463, 1704; vol. IV., Part I., pp. 868-869; Addenda, vol. I., No. 390. London, 1864 *et seq.*: H.M. Stationery Office. Page, *loc. cit.*, p. 133.

<sup>18</sup> Account of 1543, February 16, Exchequer Accounts, Bundle 60, No. 10; the large guns only were cast—for instance, by Peter Baude, the brothers John and Robert Owen and the Italian Arcanus—but they were of bronze; the smaller guns were made of wrought iron.

<sup>19</sup> Calendar of the Patent Rolls, Elizabeth, p. 42. London, 1939: H.M. Stationery Office.



of what type these guns were nor how many of them were manufactured.<sup>20</sup>

There is, however, one definite improvement which dated from round about that time. In the records of gun-founding in England previous to 1543, a distinction is constantly made between guns, *i.e.*, the barrels, and their chambers, which were detachable. But after 1543 no such distinction is made when guns of cast iron are mentioned. From this fact we may assume that the later iron guns were cast in one piece, like bronze guns. Evidently the method of casting bronze guns was applied to the founding of iron ones, first by the metal-founder Peter Baude together with Ralph Hogge, who was taught this method by Baude. These later guns were still cast hollow; they were not solid and bored afterwards, for the process of boring them was a novelty when it was applied to iron guns in Sussex in the seventeenth century.<sup>21</sup>

The first large order for making iron guns of which we have more exact knowledge was given to Levet in 1545. When, in February, 1545, a Scottish invasion was imminent, the need of artillery became more urgent than ever. So Levet was ordered to make 120 iron guns and a large amount of gun-shot. Their manufacture took nearly two years. Some of these guns went to the fortress of Portsmouth, others to the Isle of Wight. In the list of the ordnance placed at the defences of Portsmouth, dated February 16, 1547, four "sakers" of cast iron "of Parson Levett's making" are mentioned. "Sakers" were guns of the smaller type of Tudor ordnance, having an average weight of 1400 lb., *i.e.*, they were not much bigger than the guns cast at Newbridge in 1509. In the list of 1547 the guns of Levet's making were the only cast-iron guns of English manufacture; the others were imported from Flanders.<sup>22</sup>

The manufacture of large cannon such as heavy siege guns required a larger quantity of cast iron than could be produced in the comparatively small furnaces of the time. This demand led to the building of a double furnace in the Forest of Worth, west of Ashdown Forest. Worth and Sheffield belonged to Thomas Seymour, Duke of Norfolk, until his attainder for high treason in 1546, when his property in Sussex became forfeited to the Crown. On December 27, William Levet was commissioned to oversee the Duke's ironworks and mines.<sup>23</sup> Under his supervision a double

<sup>20</sup> R. Holinshed, "Chronicles," vol. III., Part II., p. 960. J. Starkie Gardner, *Archæologia*, 1898, vol. 56, p. 137. Ffoulkes, *loc. cit.*, pp. 72-73, 111. J. Stow ("The Annales or Generall Chronicle of England," p. 584, 1615) is the only one who called these guns "mortar pieces."

<sup>21</sup> This fact, mentioned by Straker (*loc. cit.*, p. 157), contradicts Salzman's assumption (*loc. cit.*, p. 165) that guns were being bored as early as 1543.

<sup>22</sup> Acts of the Privy Council, New Series I., Nos. 214, 218, 253. Letters and Papers, Henry VIII., vol. XX., Part II., Nos. 140, 520, 912; vol. XXI., Part II., No. 449. State Papers Domestic, 10/1, No. 20.

<sup>23</sup> Letters and Papers, Henry VIII., vol. XXI., Part II., No. 618.



furnace was erected at Worth in 1547; <sup>24</sup> it was the first of that kind in England known to us. A double furnace consisted of a pair of furnaces standing side by side and combined in a single structure.

Double furnaces were a rarity. The first one known was erected in 1452 by a Hungarian, named Orban, when the Turkish Sultan Mohamed II. gave orders to produce heavy siege guns for the siege of Constantinople.<sup>25</sup>

In 1574, there were two other double furnaces in Sussex. They were at Newbridge in Ashdown Forest and in the parish of North Chapel, probably at Frith.<sup>26</sup>

In the early seventeenth century Louis de Geer, who had emigrated from the Netherlands because of religious persecution, erected at Finspong in Sweden a double furnace for casting heavy iron guns for King Gustav Adolf's artillery, to which the King owed so much of his success in the Thirty Years' War.<sup>27</sup>

As guns were exported in large quantities from Sussex to the Netherlands at the end of the sixteenth century, the idea of the double furnace for casting heavy iron cannon may have come from England. From the Netherlands it was introduced into Sweden, and apparently into Western Germany also. The first German double furnace known to us was erected at Asslar, west of Wetzlar, in 1604; it served for casting iron guns for the Netherlands.<sup>28</sup> Double furnaces were used in Périgord in France also, when cannon-founding was established there with the aid of workmen brought over from England.<sup>29</sup>

The double furnace first used for casting large iron cannon in Sussex appears to have exercised a widespread influence on the cannon foundries on the Continent.

The first products of the double furnace in Worth Forest are known to us from an inventory of January 22, 1549. There were smaller guns, such as sakers, minions and falcons, and heavy guns also, *e.g.*, fourteen culverins and sixteen demi-culverins.<sup>30</sup> They were  $2\frac{1}{2}$  to  $3\frac{1}{2}$  times as large as the guns that had been cast formerly, for culverins had an average weight of 4840 lb., a length of 10 ft. 11 in. and a bore of 5.2 in., and demi-culverins had a weight of 3400 lb. and a bore of 4.0 in. Apart from these guns left at the foundry,

<sup>24</sup> Straker, *loc. cit.*, p. 81.

<sup>25</sup> Ffoulkes, *loc. cit.*, pp. 13-14.

<sup>26</sup> Straker, *loc. cit.*, pp. 429, 460.

<sup>27</sup> O. Johansen, "Geschichte des Eisens," pp. 99-100 (with ground plan of a Swedish double furnace, reproduced from T. C. Garnei's book on the Swedish furnace). Düsseldorf, 1925: Verlag Stahleisen m.b.H.

<sup>28</sup> The guns cast for the Dutch were of various types weighing from 1500 to 5400 lb.; they were still cast hollow. See H. Schubert, "Die Eisenindustrie im Gebiete der mittleren Lahn und des Vogelsberges. Vom Ursprung und Werden der Buderus'schen Eisenwerke Wetzlar," vol. I., pp. 97-98. München, 1938: F. Bruckmann.

<sup>29</sup> Rhys Jenkins, "The Rise and Fall of the Sussex Iron Industry," *Transactions of the Newcomen Society*, 1920, vol. I., pp. 22-23.

<sup>30</sup> Straker, *loc. cit.*, p. 462.

others had been cast which were sent to Southwark. Probably they were the "iron pieces" made by Levet for the King's use in 1547-49.<sup>31</sup>

When William Levet died in March, 1554, he was succeeded by his servant Ralph Hogge, who built "Hogge House" at Buxted, where he lived until his death in 1585.<sup>32</sup> During his long career as an iron-founder Ralph Hogge produced a great number of guns and much munitions, delivered principally to the Office of the Ordnance in the Tower. In 1575-80 one of his factors was in charge of 230 tons of iron ordnance, 231 tons of wrought iron, 101 tons of sowes, 33 tons of iron shot, all manufactured at Hogge's ironworks.<sup>33</sup>

In 1567 Queen Elizabeth granted Hogge the monopoly of exporting "cast iron ordnance with gunstones" to foreign countries, provided that they were not required by the Office of the Ordnance.<sup>34</sup> This privilege was infringed by others, who set up gun foundries in Sussex. In 1573 there were six such foundries, apart from Hogge's at Oldlands; one of them, at Mayfield, was the property of the famous Thomas Gresham. From Hogge's complaint against this infringement we know into which countries ordnance was exported; they were Denmark, Flanders, France, Holland, Sweden, Spain.<sup>35</sup> The exported guns were of every type, from falconets weighing 500 lb. to demi-culverins, but they were mostly of the smaller type. In South Wales there was a furnace which had been producing cast-iron ordnance since 1596; it was at Pentyrch, near Cardiff, and belonged to Edmund Mathew of Radyr. He was accused of having sent ordnance to Amsterdam, Danzig and Denmark in 1601-5 without a licence, but he admitted to exporting to Holland only.<sup>36</sup>

Apart from ordnance exported to the Continent, large quantities went to English ports such as London, Bristol, Plymouth, Portsmouth, Southampton. It was mostly used for the defence of the country and for the armament of warships, and enabled the British Navy to gain the glorious victories of the Elizabethan era.

The English iron industry was well able to export guns of cast iron during the latter part of the sixteenth century instead of importing them as in the years before. The demand for English iron cannon in the European market lasted well into the seventeenth century, when it was curtailed by supplies from the newly erected gun foundries in Sweden and Westphalia.<sup>37</sup>

<sup>31</sup> Acts of the Privy Council, New Series, vol. II., Nos. 77, 94, 214, 235. Public Record Office, Miscellaneous Books, No. 256, 87, No. 257, 84.

<sup>32</sup> Straker, *loc. cit.*, pp. 147, 398; "Sussex Notes and Queries," vol. V., p. 190.

<sup>33</sup> Public Record Office, Chancery Proceedings, Elizabeth, K5, No. 30.

<sup>34</sup> Public Record Office, Chancery Proceedings, Elizabeth, G13, No. 54.

<sup>35</sup> Ffoulkes, *loc. cit.*, p. 73. Straker, *loc. cit.*, pp. 150-152.

<sup>36</sup> Exchequer Special Commissions, 7th James I., November 23.

<sup>37</sup> British Museum, Harleian MS., 6850, No. 42. For the effect of Swedish competition upon English gun-founding, see Straker, *loc. cit.*, pp. 162-163.

The superior position held by English iron cannon in the European market was mainly due to the efforts of Ralph Hogge and his master William Levet since 1543. This date marks the beginning of a continuous casting of iron guns on a large scale and by an improved method adapted from the founding of non-ferrous metals. At the same time it was a revival based upon the old tradition of iron-casting which had never completely died out in Sussex since the days of the French founders and gunners who had introduced it round about 1490. It was this tradition which first led to the casting of iron guns at Newbridge in 1508 and 1509 by the French foundryman Pauncelett Symart with the help of the English gunner Henry Craymer. Their product was the first cast-iron cannon made in England which can be definitely dated and located.

## THE INFLUENCE OF TIN ON ALLOY STEELS.<sup>1</sup>

By G. R. BOLSOVER AND S. BARRACLOUGH (MESSRS. SAMUEL FOX  
& Co., LTD.).

### SUMMARY.

The authors have investigated the effect of tin, in amounts not exceeding about 0.5%, on the mechanical properties and particularly the notched-bar impact values of seven of the most used alloy steels, with relatively high and low phosphorus contents, a plain carbon steel being included as a basis of comparison; the influence of molybdenum in conjunction with tin was also noted. The steels comprised a 0.35% carbon steel, a manganese-molybdenum steel, a 3½% nickel and a 3% nickel-chromium steel suitable for oil-hardening, two 3% nickel-chromium-molybdenum oil-hardening steels, one with 0.20–0.25% and the other with 0.4–0.5% of molybdenum, a 3% chromium-molybdenum oil-hardening and nitriding steel and a 4¼% nickel-chromium-molybdenum case-hardening steel.

The general effect of tin on the properties of the steels in the hardened and tempered condition and of molybdenum in counteracting that of a high tin content is shown, and further data indicate the influence of tin on the nitriding steel after a blank nitriding operation and on a case-hardening steel in the quenched condition.

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AN instance of a cast of alloy steel with impact values lower than normal was encountered, and an investigation into the cause of this brittleness led to the conclusion that this might be due to a content of tin greater than would usually be present.

In view of this a careful search was made to determine what data had been published regarding the influence of tin on steel, but this revealed that very little information was available relative to the influence of this element on carbon steels and none concerning its effect on alloy steels. Consequently, it was decided to make a brief general survey of the influence of tin on some of the alloy steels most commonly employed.

The steels selected were the manganese-molybdenum, 3½% nickel and 3% nickel-chromium qualities as representative of steels for oil-hardening and tempering, with a 0.35% carbon steel, without any alloying element, included as a basis for comparison. In addition, a 4¼% nickel-chromium case-hardening steel was included.

Series of these types of steel were accordingly prepared in a 35 kVA. high-frequency furnace of 18 lb. capacity, of the Ajax-

<sup>1</sup> Received December 12, 1941.

TABLE I.—0.35% Carbon Steel.

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Sn. %.
C1	0.37	0.75	0.22	0.019	0.020	0.07	Trace	0.015
C2	0.36	0.76	0.23	0.020	0.019	0.07	„	0.11
C3	0.34	0.76	0.205	0.019	0.018	0.07	„	0.195
C4	0.34	0.75	0.20	0.021	0.020	0.08	„	0.27
C5	0.37	0.75	0.22	0.020	0.020	0.08	„	0.385
C6	0.34	0.75	0.205	0.020	0.022	0.09	„	0.47
C7	0.33	0.78	0.24	0.020	0.045	0.09	„	0.10
C8	0.32	0.62	0.215	0.019	0.036	0.09	„	0.18
C9	0.35	0.82	0.24	0.019	0.047	0.09	„	0.33
C10	0.29	0.62	0.20	0.021	0.036	0.08	„	0.11
C11	0.30	0.66	0.215	0.020	0.036	0.08	„	0.275

 $\frac{7}{8}$ -in. dia. bars.

(a) O.Q. 850° C., T. 650° C., O.Q.

(b) O.Q. 850° C., T. 650° C., furnace-cooled.

(c) O.Q. 850° C., T. 650° C., furnace-cooled, re-tempered 650° C. and O.Q.

(d) A.C. 850° C.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $4\sqrt{A}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
								Average.
C1 (a)	42.1	31.0	29.5	66.0	58	58	53	55.3
(b)	41.4	27.8	30.5	66.0	59	55	62	58.7
(c)	...	...	...	...	69	83	71	74.3
(d)	41.6	26.8	28.5	57.2	54	57	49	53.3
C2 (a)	44.3	30.6	29.0	63.6	59	62	50	57.0
(b)	42.5	29.9	28.0	63.6	31	34	30	31.7
(c)	...	...	...	...	60	80	60	66.7
(d)	43.3	29.2	28.0	54.8	36	36	33	35.0
C3 (a)	43.2	30.8	28.0	63.6	56	55	47	52.7
(b)	42.1	30.6	29.0	61.6	20	19	19	19.3
(c)	...	...	...	...	48	46	42	45.3
(d)	42.2	28.2	28.0	52.4	22	25	25	24.0
C4 (a)	44.3	33.0	28.0	63.6	28	24	27	26.3
(b)	42.8	29.6	25.5	57.2	11	12	12	11.7
(c)	...	...	...	...	34	34	35	34.3
(d)	42.8	29.2	27.5	54.4	23	22	20	21.7
C5 (a)	45.2	31.1	26.0	59.2	24	24	19	22.3
(b)	44.6	31.1	25.0	54.8	8	6	9	7.7
(c)	...	...	...	...	23	31	27	27.0
(d)	45.1	30.5	28.0	54.4	13	13	13	13.0
C6 (a)	44.5	32.6	26.0	54.8	21	24	23	22.7
(b)	42.9	30.8	26.0	52.4	10	9	6	8.3
(c)	...	...	...	...	27	27	29	27.7
(d)	43.8	30.6	26.5	54.4	15	17	15	15.7



TABLE I.—Continued.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on 4√A. %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
							Average.	
C7 (a)	45.1	31.8	26.5	63.6	52	54	56	54.0
(b)	43.9	31.1	27.0	61.6	26	32	27	28.3
(c)	...	...	...	...	60	59	61	60.0
(d)	41.2	27.1	29.0	54.8	26	28	29	27.7
C8 (a)	40.6	29.1	30.0	66.0	49	55	48	50.7
(b)	39.6	28.5	30.0	66.0	30	30	28	29.3
(c)	...	...	...	...	53	48	57	52.7
(d)	40.2	28.7	30.0	57.2	31	31	25	28.3
C9 (a)	46.4	32.8	25.5	59.2	19	21	26	22.0
(b)	45.7	32.6	24.5	57.2	8	6	5	6.3
(c)	...	...	...	...	19	23	21	21.0
(d)	43.4	28.2	25.0	49.6	10	11	11	10.7
C10 (a)	38.9	27.4	32.0	66.0	77	79	55	70.3
(b)	36.8	25.3	32.0	63.6	64	68	65	65.7
(c)	...	...	...	...	92	96	75	87.7
(d)	38.3	25.1	31.0	57.2	49	49	45	47.7
C11 (a)	40.9	28.6	29.0	63.6	42	44	47	44.3
(b)	39.9	27.3	30.5	63.6	24	24	25	24.3
(c)	...	...	...	...	41	45	48	44.7
(d)	40.2	27.2	29.0	57.2	31	28	34	31.0

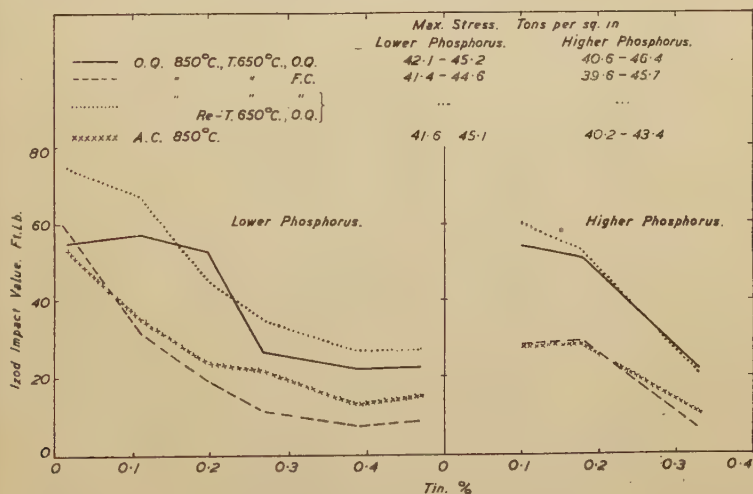


FIG. 1.—0.35% Carbon Steel.

TABLE II.—*Manganese-Molybdenum Steel.*

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Sn. %.
M1	0.36	1.46	0.225	0.019	0.022	0.08	Trace	0.26	0.039
M2	0.35	1.45	0.205	0.021	0.020	0.08	„	0.27	0.127
M3	0.34	1.46	0.185	0.021	0.021	0.08	„	0.26	0.18
M4	0.35	1.49	0.225	0.019	0.023	0.08	„	0.27	0.32
M5	0.34	1.50	0.245	0.022	0.024	0.08	„	0.25	0.44
M6	0.35	1.51	0.225	0.019	0.023	0.08	„	0.25	0.54
M7	0.38	1.41	0.215	0.024	0.045	0.09	„	0.28	0.13
M8	0.35	1.53	0.235	0.021	0.048	0.07	„	0.27	0.155
M9	0.35	1.53	0.235	0.020	0.046	0.08	„	0.25	0.16
M10	0.33	1.52	0.235	0.019	0.044	Trace	0.01	0.29	0.17
M11	0.38	1.44	0.225	0.020	0.044	0.07	Trace	0.26	0.22
M12	0.34	1.55	0.205	0.020	0.046	0.06	„	0.26	0.315
M13	0.33	1.45	0.235	0.018	0.043	0.09	0.01	0.38	0.12

 $\frac{3}{8}$ -in. dia. bars.

(a) O.Q. 850° C., T. 650° C., O.Q.

(b) O.Q. 850° C., T. 650° C., furnace-cooled.

(c) O.Q. 850° C., T. 650° C., furnace-cooled, re-tempered 650° C. and O.Q.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on 4 V.A. %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
							Average.	
M1 (a)	55.2	49.0	21.5	59.2	69	70	72	70.3
(b)	52.3	45.0	22.5	61.6	66	66	69	67.0
(c)	...	...	...	...	66	66	67	66.3
M2 (a)	55.1	47.2	22.5	61.6	67	68	68	67.7
(b)	53.3	45.5	22.0	57.2	53	50	49	50.7
(c)	...	...	...	...	61	65	64	63.3
M3 (a)	56.4	50.4	22.5	59.2	64	59	62	61.7
(b)	53.4	46.9	21.5	54.8	30	31	31	30.7
(c)	...	...	...	...	64	65	62	63.7
M4 (a)	57.4	50.6	21.0	54.8	50	49	55	51.7
(b)	56.3	48.5	21.0	54.8	14	14	14	14.0
(c)	...	...	...	...	50	52	53	51.7
M5 (a)	53.9	44.8	23.0	54.8	46	45	49	46.7
(b)	53.8	45.7	22.0	49.6	13	9	9	10.3
(c)	...	...	...	...	48	...	...	...
					(Defective test-piece)			
M6 (a)	54.7	45.7	22.5	57.2	49	48	42	45.0
(b)	55.0	46.8	21.5	49.6	12	9	10	10.3
(c)	...	...	...	...	44	49	50	46.3
M7 (a)	57.7	50.2	21.0	59.2	70	71	68	69.7
(b)	55.9	47.6	21.0	54.8	26	31	25	27.3
(c)	...	...	...	...	70	68	69	69.0

TABLE II.—*Continued.*

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on 4√A. %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
							Average.	
M8 (a)	55.5	48.2	23.5	61.6	63	64	63	63.7
(b)	53.7	46.2	22.5	59.2	30	31	28	29.7
(c)	...	...	...	...	65	66	63	64.7
M9 (a)	56.1	49.0	20.0	49.6	56	55	59	57.7
(b)	54.6	48.0	22.0	57.2	18	18	18	18.0
(c)	...	...	...	...	53	53	59	55.0
M10 (a)	56.7	49.8	21.5	57.2	49	52	51	50.7
(b)	56.0	48.7	21.5	54.8	14	13	13	13.3
(c)	...	...	...	...	51	56	55	54.0
M11 (a)	57.8	51.0	20.5	54.8	44	53	51	49.3
(b)	57.0	48.7	20.5	49.6	14	13	12	13.0
(c)	...	...	...	...	53	61	49	54.3
M12 (a)	57.4	50.0	21.5	54.8	51	54	54	53.0
(b)	55.3	47.8	21.0	49.6	11	12	13	12.0
(c)	...	...	...	...	52	52	52	52.0
M13 (a)	58.6	52.3	21.0	57.2	64	68	69	67.0
(b)	57.4	50.3	20.0	52.4	37	38	38	37.7
(c)	...	...	...	...	64	61	65	63.3

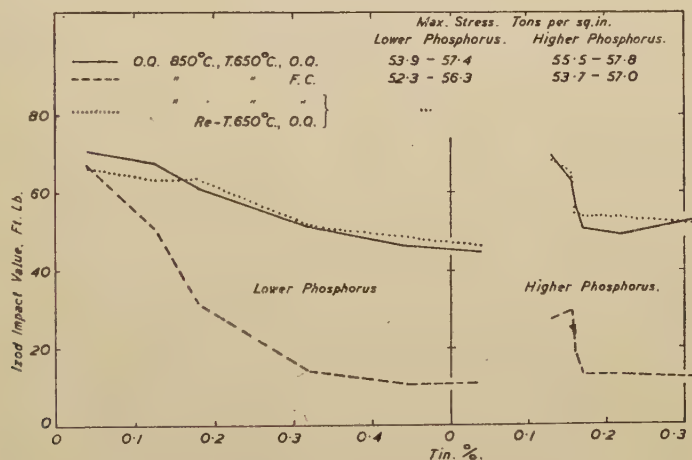


FIG. 2.—Manganese-Molybdenum Steel.

TABLE III.—3½% Nickel Oil-Hardening Steel.

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Sn. %.
N1	0.34	0.64	0.235	0.020	0.023	3.39	0.01	0.022
N2	0.37	0.68	0.25	0.018	0.024	3.30	0.01	0.105
N3	0.37	0.64	0.235	0.034	0.022	3.41	0.01	0.25
N4	0.37	0.64	0.255	0.019	0.024	3.40	0.01	0.32
N5	0.365	0.64	0.245	0.019	0.021	3.40	0.01	0.40
N6	0.335	0.64	0.245	0.018	0.022	3.38	0.01	0.50
N7	0.34	0.60	0.23	0.019	0.037	3.30	Trace	0.13
N8	0.36	0.58	0.225	0.018	0.044	3.34	Trace	0.19
N9	0.345	0.64	0.22	0.020	0.052	3.40	0.01	0.345

$\frac{7}{8}$ -in. dia. bars.

(a) O.Q. 830° C., T. 600° C., O.Q.

(b) O.Q. 830° C., T. 600° C., furnace-cooled.

(c) O.Q. 830° C., T. 600° C., furnace-cooled, re-tempered 600° C., and O.Q.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on 4√A. %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
					Average.			
N1 (a)	51.5	43.9	23.0	61.6	66	67	69	67.3
(b)	51.2	43.4	24.0	61.6	50	60	57	55.7
(c)	...	...	...	...	71	70	69	70.0
N2 (a)	54.6	47.8	21.5	59.2	50	55	50	51.7
(b)	54.5	47.8	22.5	59.2	18	16	16	16.7
(c)	...	...	...	...	56	56	57	56.3
N3 (a)	55.1	48.5	20.5	59.2	40	40	33	37.7
(b)	56.7	49.8	20.0	49.6	16	17	17	16.7
(c)	...	...	...	...	44	45	46	45.0
N4 (a)	57.6	51.4	20.0	52.4	23	23	23	23.0
(b)	58.0	51.8	20.5	52.4	13	12	12	12.3
(c)	...	...	...	...	30	32	29	30.3
N5 (a)	59.6	54.7	18.0	47.2	13	15	15	14.3
(b)	59.7	53.7	18.5	47.2	9	6	10	8.3
(c)	...	...	...	...	21	21	18	20.0
N6 (a)	59.9	54.0	16.5	44.4	10	11	15	12.0
(b)	60.6	55.2	17.0	47.2	9	12	10	10.3
(c)	...	...	...	...	18	15	17	16.7
N7 (a)	56.2	49.1	21.5	57.2	34	38	33	35.0
(b)	55.3	48.0	21.5	52.4	11	11	9	10.3
(c)	...	...	...	...	43	46	42	43.7
N8 (a)	58.4	51.6	19.0	47.2	19	20	18	19.0
(b)	58.3	51.1	18.0	42.0	6	6	9	7.0
(c)	...	...	...	...	23	21	20	21.3
N9 (a)	57.6	51.4	21.5	54.8	11	12	12	11.7
(b)	59.1	53.3	18.0	47.2	4	4	5	4.3
(c)	...	...	...	...	20	10	11	13.7

Northrup spark-gap type, producing ingots of approximately 2 in. square section, these being forged to  $\frac{7}{8}$ -in. dia. bar for heat treatment and testing. Each series of steels included a basis steel with a low tin content, the other samples having an addition of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% of tin. Further, the effect of phosphorus was investigated by the inclusion of a limited number of steels aiming at a phosphorus content of approximately 0.045%, as compared with a percentage of the order of 0.020% in the main series.

The early results were of sufficient interest to promote queries regarding the influence of molybdenum, if present, for example, in a steel of the 3% nickel-chromium type, in conjunction with a high tin content. Two series with approximately 0.2% and 0.4% of

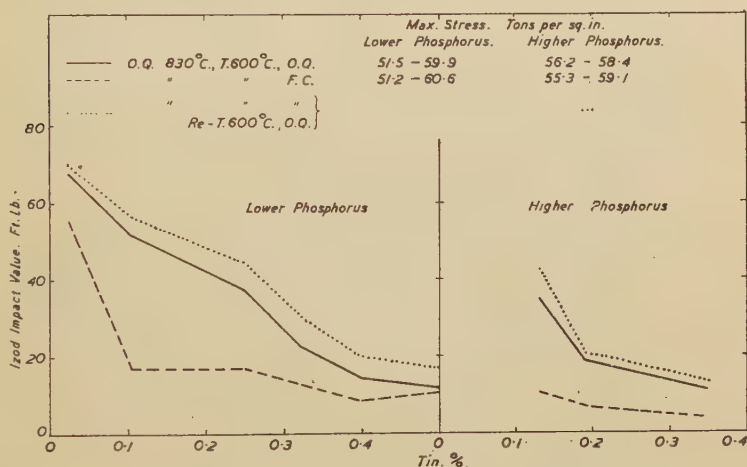


FIG. 3.— $3\frac{1}{2}\%$  Nickel Oil-Hardening Steel.

molybdenum, respectively, were therefore produced over a limited range of tin additions. In order to include a steel of the nitriding type, several steels of the 3% chromium-molybdenum quality were also made and examined in the same way.

It will be appreciated that the results recorded can be regarded as only a very general survey of the effect of the presence of tin over the alloy-steel field. It is nevertheless felt, particularly in view of the absence of other data, that the publication of these results will be of some interest and value, not only by preventing the repetition of similar work, but by indicating the direction in which further investigation may be made.

The results obtained for the various steels are recorded in Tables I. to VIII. and are also shown in the form of graphs in



TABLE IV.—3% Nickel-Chromium Oil-Hardening Steel.

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Sn. %.
S1	0.30	0.54	0.215	0.019	0.021	3.10	0.78	0.037
S2	0.30	0.52	0.22	0.018	0.023	3.08	0.73	0.11
S3	0.31	0.58	0.21	0.018	0.022	3.04	0.82	0.24
S4A	0.30	0.51	0.225	0.018	0.022	3.08	0.80	0.33
S4B	0.31	0.55	0.225	0.018	0.023	3.08	0.77	0.33
S5	0.285	0.54	0.22	0.019	0.024	3.08	0.83	0.39
S6	0.29	0.53	0.215	0.017	0.021	3.10	0.85	0.48
S7	0.31	0.57	0.235	0.019	0.040	3.08	0.73	0.092
S8	0.30	0.55	0.23	0.019	0.039	3.04	0.75	0.10
S9	0.32	0.62	0.265	0.018	0.042	3.32	0.79	0.195
S10	0.29	0.53	0.22	0.018	0.053	3.10	0.81	0.31

 $\frac{7}{8}$ -in. dia. bars.

(a) O.Q. 830° C., T. 630° C., O.Q.

(b) O.Q. 830° C., T. 630° C., furnace-cooled.

(c) O.Q. 830° C., T. 630° C., furnace-cooled, re-tempered 630° C. and O.Q.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $4\sqrt{A}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
					Average.			
S1 (a)	57.5	51.3	22.0	63.6	66	69	71	68.7
(b)	56.6	51.8	22.5	61.6	10	13	13	12.0
(c)	...	...	...	...	72	72	75	73.0
S2 (a)	59.4	52.5	21.5	59.2	40	32	29	33.7
(b)	58.6	52.4	22.0	57.2	6	10	12	9.3
(c)	...	...	...	...	46	47	50	47.7
S3 (a)	61.2	53.6	22.0	59.2	13	13	11	12.3
(b)	61.2	54.3	20.0	52.4	3	3	6	4.0
(c)	...	...	...	...	14	16	14	14.7
S4A (a)	60.6	53.9	20.0	52.4	12	13	10	11.7
(b)	61.0	54.0	22.0	52.4	7	8	10	8.3
(c)	...	...	...	...	16	13	14	14.3
S4B (a)	59.9	53.4	20.0	54.8	15	12	13	13.3
(b)	60.7	56.4	18.0	49.6	6	6	5	5.7
(c)	...	...	...	...	14	12	14	13.3
S5 (a)	62.3	56.7	19.0	49.6	8	6	9	7.7
(b)	61.0	56.1	19.5	49.6	6	5	6	5.7
(c)	...	...	...	...	11	10	12	11.0
S6 (a)	61.8	55.1	18.5	47.2	6	7	7	6.7
(b)	62.4	55.9	16.5	44.4	5	5	4	4.7
(c)	...	...	...	...	8	8	9	8.3

TABLE IV.—*Continued.*

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $A\sqrt{4}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.				
S7 (a)	59.2	51.6	23.5	59.2	16	17	16	Average.	
	(b)	60.7	51.8	21.5	47.2	3	3	3	16.3
	(c)	...	...	...	...	29	35	30	3.0
S8 (a)	58.1	51.8	22.0	61.6	18	20	19	19.0	
	(b)	59.8	51.9	22.0	57.2	4	3	4	3.7
	(c)	...	...	...	...	28	30	29	29.0
S9 (a)	61.8	54.8	18.5	49.6	5	6	3	4.7	
	(b)	64.2	56.2	16.5	42.0	2	2	2	2.0
	(c)	...	...	...	...	7	7	7	7.0
S10 (a)	60.7	54.5	20.0	49.6	5	7	9	7.0	
	(b)	60.7	55.8	19.5	42.0	4	3	3	3.3
	(c)	...	...	...	...	7	4	6	5.7

Figs. 1 to 8. As will be appreciated, in the manufacture of nearly seventy different samples, slight variations from the composition required are liable to occur. All the steels, however, were tested and all the results, even though certain casts had one or more elements outside the desired range of composition, are reported, but for the graphs only those steels within fairly narrow limits

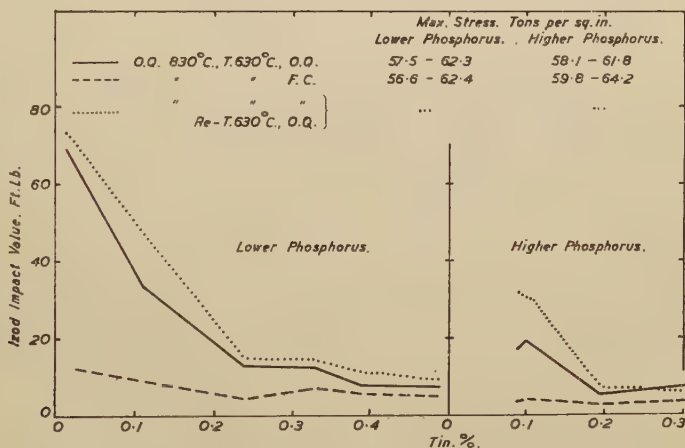


FIG. 4.—3% Nickel-Chromium Oil-Hardening Steel.

TABLE V.—3% *Nickel-Chromium-Molybdenum Oil-Hardening Steel*  
(0.20–0.25% *Molybdenum*).

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Sn. %.
L1	0.35	0.65	0.20	0.022	0.023	3.10	0.82	0.24	0.037
L2	0.30	0.62	0.21	0.021	0.022	3.10	0.83	0.23	0.12
L3	0.31	0.65	0.19	0.019	0.020	3.08	0.81	0.22	0.22
L4	0.32	0.67	0.16	0.019	0.046	3.08	0.81	0.21	0.044
L5	0.34	0.65	0.18	0.020	0.046	3.10	0.79	0.23	0.105
L6	0.31	0.63	0.20	0.022	0.043	3.08	0.79	0.24	0.22

$\frac{7}{8}$ -in. dia. bars.  
 (a) O.Q. 830° C., T. 630° C., O.Q.  
 (b) O.Q. 830° C., T. 630° C., furnace-cooled.  
 (c) O.Q. 830° C., T. 630° C., furnace-cooled, re-tempered 630° C. and O.Q.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on 4√A. %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
							Average.	
L1 (a)	62.9	55.9	19.0	57.2	58	58	59	58.3
(b)	62.1	55.7	21.0	57.2	53	54	56	54.3
(c)	...	...	...	...	55	56	56	55.7
L2 (a)	63.9	58.1	20.5	59.2	47	50	51	49.3
(b)	63.0	56.9	20.0	57.2	46	49	45	46.7
(c)	...	...	...	...	60	55	53	56.0
L3 (a)	63.6	57.9	18.5	52.4	43	45	49	45.7
(b)	66.0	58.6	19.5	52.4	39	40	38	39.0
(c)	...	...	...	...	56	52	48	52.0
L4 (a)	62.3	55.9	20.0	59.2	55	54	54	54.3
(b)	62.3	55.1	20.5	54.8	34	34	35	34.3
(c)	...	...	...	...	62	59	53	58.0
L5 (a)	64.6	59.2	18.0	52.4	49	50	50	49.7
(b)	63.3	57.2	19.5	52.4	22	20	18	20.0
(c)	...	...	...	...	54	59	50	54.3
L6 (a)	64.7	57.0	19.0	52.4	36	32	37	35.0
(b)	65.9	58.3	18.5	47.2	15	15	15	15.0
(c)	...	...	...	...	45	45	44	44.7

have been selected. To decide whether a steel should be included in a graph, judgment was based more on the tensile strength than on detailed composition, provided that the latter was within reasonable limits of that desired. In view of this, and in order to indicate readily the degree of variation, the range of maximum stress for each type of steel in each condition of heat treatment has been stated on the graphs.

The general scheme of heat treatment has been as follows :

For steels to be hardened and tempered—

(1) Oil-quench and temper, followed by oil-quenching.

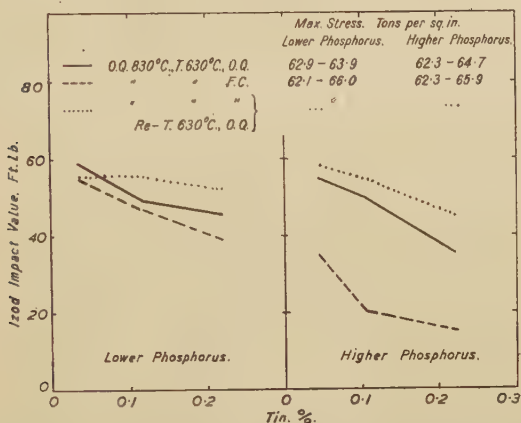


FIG. 5.—3% Nickel-Chromium-Molybdenum Oil-Hardening Steel (0.20-0.25% Molybdenum).

(2) Oil-quench and temper, followed by furnace-cooling. (Furnace-cooling occupies approximately 9 hr. from the tempering temperature to the temperature of 300° C.)

(3) Oil-quench and temper, followed by furnace-cooling, followed by a re-temper at the same tempering temperature and oil-quenching.

Additions to this programme were made in the case of the plain carbon steel by including tests in the normalised condition, and in the case of the 3% chromium-molybdenum steel by including tests after a dummy nitriding treatment.

The case-hardening steel was tested as oil-quenched from 760° C. and tempered at 150° C.

TABLE VI.—3% Nickel-Chromium-Molybdenum Oil-Hardening Steel (0.40–0.50% Molybdenum).

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Sn. %.
T1	0.36	0.67	0.205	0.020	0.021	3.08	0.85	0.46	0.039
T2	0.32	0.67	0.20	0.021	0.018	3.10	0.77	0.48	0.11
T3	0.30	0.66	0.19	0.021	0.021	3.10	0.81	0.46	0.205
T4	0.32	0.67	0.20	0.019	0.047	3.10	0.84	0.46	0.042
T5	0.31	0.63	0.19	0.020	0.044	3.06	0.80	0.48	0.13
T6	0.31	0.62	0.15	0.019	0.044	3.10	0.82	0.46	0.22

$\frac{7}{8}$ -in. dia. bars.  
 (a) O.Q. 830° C., T. 630° C., O.Q.  
 (b) O.Q. 830° C., T. 630° C., furnace-cooled.  
 (c) O.Q. 830° C., T. 630° C., furnace-cooled, re-tempered 630° C. and O.Q.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $4\sqrt{A}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
					Average.			
T1 (a)	68.6	61.3	20.0	59.2	46	46	51	47.7
(b)	69.3	62.4	18.5	52.4	36	38	38	37.3
(c)	...	...	...	...	50	54	54	52.7
T2 (a)	67.6	61.6	20.0	54.8	46	46	46	46.0
(b)	67.8	62.4	19.0	54.2	35	37	39	37.0
(c)	...	...	...	...	49	46	47	47.3
T3 (a)	67.2	61.1	18.5	54.8	45	43	46	44.7
(b)	68.6	61.0	19.0	52.4	26	29	33	29.3
(c)	...	...	...	...	47	48	45	46.3
T4 (a)	66.2	60.1	21.0	57.2	48	47	44	46.3
(b)	66.0	59.8	19.0	54.8	19	19	18	18.7
(c)	...	...	...	...	57	55	55	55.7
T5 (a)	68.0	62.0	19.5	57.2	31	34	37	34.0
(b)	66.8	59.6	20.5	54.8	19	14	16	16.3
(c)	...	...	...	...	39	42	45	42.0
T6 (a)	68.8	63.8	19.5	54.8	25	26	29	26.7
(b)	67.8	61.2	20.5	54.8	19	17	15	17.0
(c)	...	...	...	...	38	37	37	37.3



*Commentary.*

On all the hardened and tempered steels examined, the influence of the presence of tin at even 0.1% is shown on notched-bar impact tests. It is interesting to note in the case of the basis carbon steel that this effect is not so marked in the condition oil-quenched after tempering as it is in the normalised condition. On the alloy steels the effect of tin additions appears to be counteracted very appreciably by the addition of molybdenum, as shown by the results on the manganese-molybdenum steel and on the 3% nickel-chromium-molybdenum steels, comparing these with either the 3% nickel or the 3% nickel-chromium (without molybdenum) steels.

The higher-phosphorus steels, in general, give lower results than the lower-phosphorus steels, but on the data available this appears to be more in the nature of a lowering of the impact value owing to the phosphorus content rather than due to any increasing effect

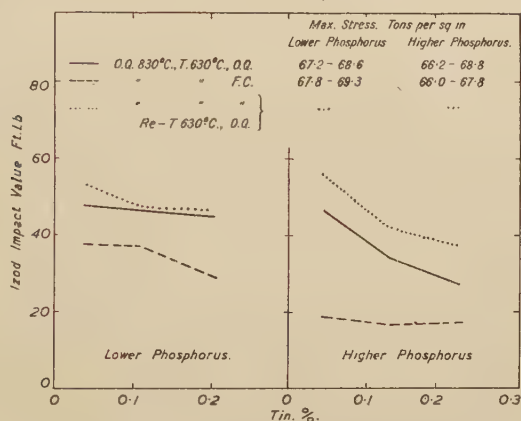


FIG. 6.—3% Nickel-Chromium-Molybdenum Oil-Hardening Steel (0.4–0.5% Molybdenum).

of tin on the high-phosphorus as compared with the low-phosphorus steels.

The effect of tin on the nitriding steel again appears to be counterbalanced to some extent by the addition of molybdenum, but the lowering of the impact value after nitriding in the presence of tin is very marked.

The 4½% nickel-chromium case-hardening steel suffers only a slight decrease of impact value up to 0.15% of tin, but with higher contents the values fall very seriously.

Thanks are due to Dr. T. Swinden and his staff in the Central Research Department of the United Steel Companies, Ltd., for supplying the desired spark-gap ingots.

TABLE VII.—3% Chromium-Molybdenum Oil-Hardening and Nitriding Steel.

Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Sn. %.
R1	0.30	0.52	0.16	0.021	0.019	0.10	3.18	0.54	0.052
R2	0.28	0.48	0.16	0.020	0.023	0.10	3.10	0.55	0.15
R3	0.26	0.46	0.16	0.021	0.016	0.11	3.18	0.54	0.21

$\frac{7}{8}$ -in. dia. bars.

(a) O.Q. 900° C., T. 620° C., O.Q.

(b) O.Q. 900° C., T. 620° C., furnace-cooled.

(c) O.Q. 900° C., T. 620° C., furnace-cooled, re-tempered 620° C. and O.Q.

(d) O.Q. 900° C., T. 620° C., O.Q., reheated 500° C. 72 hr., and furnace-cooled.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $4\sqrt{A}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
R1 (a)	67.4	61.5	20.0	61.6	59	60	63	Average. 60.7
	(b) 67.8	59.8	18.5	61.6	57	62	71	63.3
	(c) ...	...	...	...	64	66	65	65.0
	(d) 68.0	63.2	19.0	61.6	60	61	60	60.3
R2 (a)	68.1	61.6	18.5	61.6	53	54	55	54.0
	(b) 67.1	59.7	18.0	59.2	34	41	35	36.7
	(c) ...	...	...	...	65	66	64	65.0
	(d) 66.8	59.4	18.5	61.6	30	34	33	32.3
R3 (a)	66.6	59.4	14.5	44.4	42	39	39	40.0
	(b) 66.0	58.6	17.0	54.8	5	5	5	5.0
	(c) ...	...	...	...	51	57	57	55.0
	(d) 64.6	58.8	16.5	52.4	5	6	6	5.7

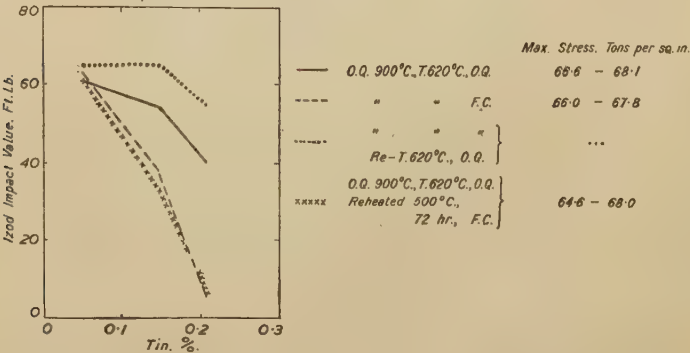


FIG. 7.—3% Chromium-Molybdenum Steel.

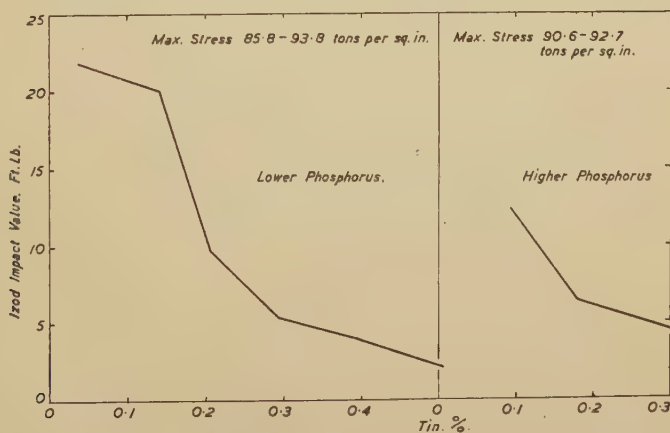
TABLE VIII.— $4\frac{1}{4}\%$  Nickel-Chromium-Molybdenum Case-Hardening Steel.

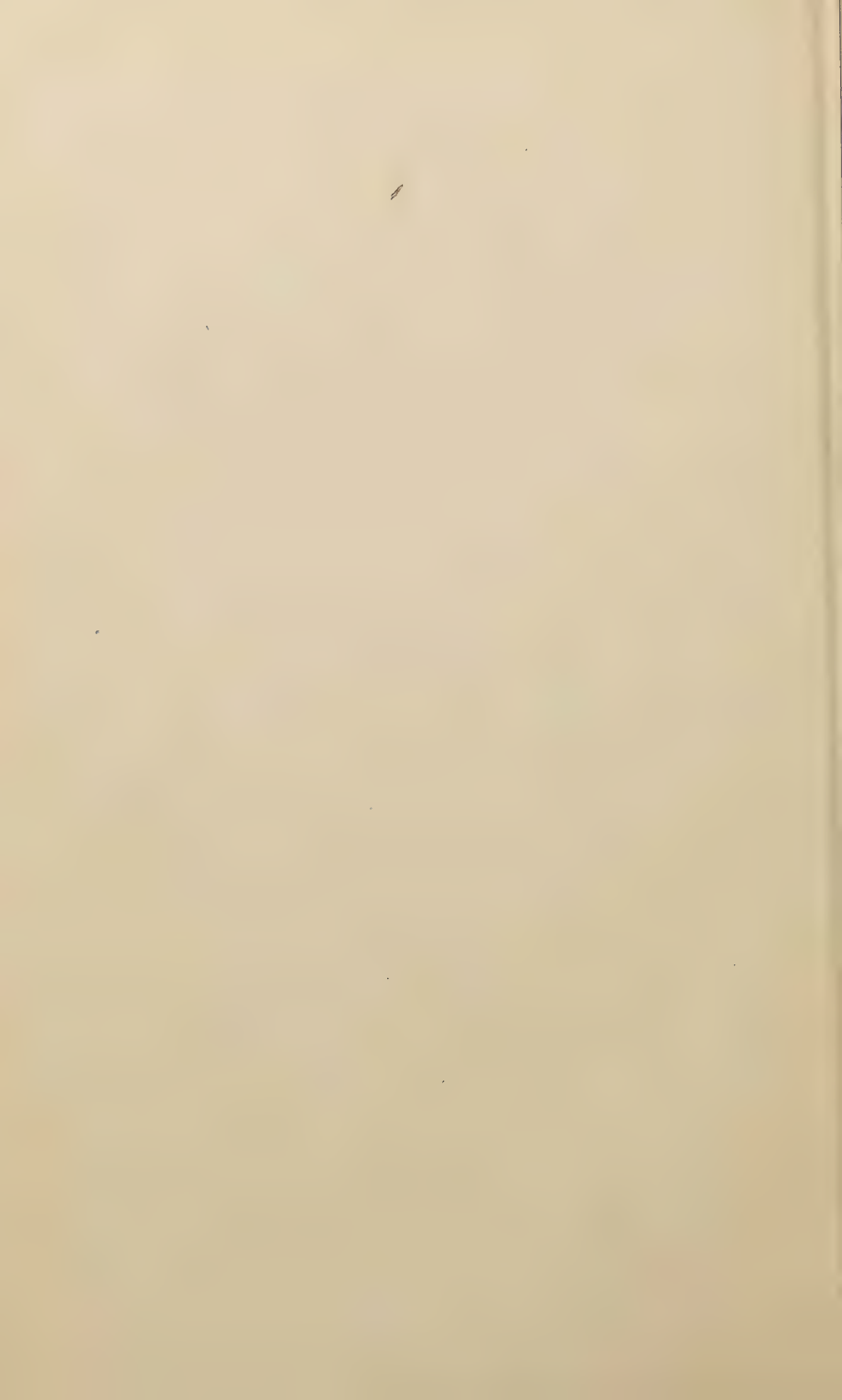
Mark.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Sn. %.
H1	0.17	0.43	0.20	0.019	0.024	4.34	1.10	0.12	0.034
H2	0.18	0.45	0.20	0.019	0.023	4.32	1.11	0.13	0.14
H3	0.17	0.44	0.19	0.021	0.022	4.38	1.12	0.12	0.205
H4	0.18	0.43	0.19	0.024	0.020	4.32	1.16	0.125	0.295
H5	0.15	0.41	0.20	0.020	0.021	4.34	1.08	0.135	0.395
H6	0.15	0.43	0.20	0.020	0.022	4.38	1.11	0.12	0.505
H7	0.18	0.42	0.21	0.022	0.044	4.38	1.10	0.12	0.095
H8	0.18	0.42	0.215	0.020	0.045	4.32	1.07	0.13	0.18
H9	0.16	0.38	0.165	0.019	0.044	4.30	1.07	0.145	0.31
H10	0.18	0.42	0.215	0.019	0.046	4.36	1.11	Trace	0.295

 $\frac{7}{8}$ -in. dia. test-bar.

O.Q. 860° C., O.Q. 760° C., T. 150° C.

Mark and Condition.	Max. Stress. Tons per sq. in.	Yield Point. Tons per sq. in.	Elongation on $4\sqrt{A}$ . %.	Reduction of Area. %.	Izod Impact Value. Ft.lb.			
							Average.	
H1	92.3	86.7	14.5	47.2	21	21	23	21.7
H2	90.3	85.6	15.0	47.2	17	20	23	20.0
H3	91.9	83.1	14.5	44.4	9	10	10	9.7
H4	93.8	89.8	13.5	44.4	6	5	5	5.3
H5	85.8	76.4	13.5	44.4	4	4	4	4.0
H6	90.9	86.0	13.0	42.0	2	2	2	2.0
H7	92.7	89.5	14.5	42.0	12	12	13	12.3
H8	90.6	87.2	14.0	44.4	6	6	7	6.3
H9	92.2	86.0	15.0	47.2	4	5	4	4.3
H10	94.1	91.2	14.0	39.2	3	3	3	3.0

FIG. 8.— $4\frac{1}{4}\%$  Nickel-Chromium-Molybdenum Case-Hardening Steel.



# THE CRYSTAL STRUCTURES OF Fe, FeO AND Fe<sub>3</sub>O<sub>4</sub> AND THEIR INTERRELATIONS.\*

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## SUMMARY.

A simple relation is shown to exist between the lattice dimensions of the three phases of the iron-oxygen system:  $\alpha$ -iron (Fe), wüstite (FeO) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The close connection between the three structures, which are all cubic, explains why a comparatively easy transition from Fe to FeO, from Fe to Fe<sub>3</sub>O<sub>4</sub> and from FeO to Fe<sub>3</sub>O<sub>4</sub> is possible under practical oxidising conditions implying limited access of oxygen. While the transition Fe  $\rightarrow$  FeO is considered as a true oxidation, the change FeO  $\rightarrow$  Fe<sub>3</sub>O<sub>4</sub> is not, because the number of oxygen ions per crystal volume remains constant, only iron being lost. The wüstite range of solid solutions is discussed from the same aspect; the omission of ferrous Fe<sup>++</sup> ions from lattice points under partial replacement by ferric Fe<sup>+++</sup> ions is preparatory to the change-over to the Fe<sub>3</sub>O<sub>4</sub> structure. The linear decrease of lattice spacing of wüstite with increasing oxygen content, as found by Jette and Foote, is utilised. It is observed that the lattice parameter of the Fe<sub>3</sub>O<sub>4</sub> unit cell is in direct linear continuation of the same decrease. The ionic replacements within the lattice during this process are considered numerically in some detail; they finally lead to a distribution of ions agreeing with the known spinel structure.

The structure of  $\gamma$ -iron is intimately connected with that of FeO, a fact which is corroborated by comparing the atomic volumes of all the phases concerned. It is suggested by this comparison that similar relations exist between  $\alpha$ -Fe and Fe<sub>3</sub>O<sub>4</sub> on the one hand and  $\gamma$ -Fe and FeO on the other, each pair of phases being thus fundamentally associated, and that the  $\gamma$ - $\alpha$  change at 906° C. is coupled with the decomposition of FeO at 570° C.: [4FeO  $\rightarrow$  Fe + Fe<sub>3</sub>O<sub>4</sub>].

The results of some X-ray tests on layers of scales formed on pure iron are included mainly to illustrate two points:

(1) The decrease of the wüstite lattice constants with decreasing iron content.

(2) The effect on the structure of the scale of exposing either  $\alpha$ -Fe or  $\gamma$ -Fe to oxidising conditions.

The latter preliminary experiments revealed the innermost layer of scale to be pure wüstite if formed at, and quenched from, temperatures above A<sub>3</sub>, and wüstite plus magnetite below A<sub>3</sub>, the proportion of magnetite increasing with decreasing temperature.

The facts discussed have a bearing on the problem of the corrosion resistance of steel.

## (1) INTRODUCTION.

It has been established by X-ray tests that the oxidation of pure iron and ferritic steels at elevated temperatures under conditions implying a restricted supply of oxygen or short-time heating produces the two phases FeO (wüstite) and Fe<sub>3</sub>O<sub>4</sub> (magnetite).  $\alpha$ -iron

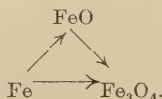
\* Received June 19, 1942.



from the parent metal is liable to be present as a third phase. On the other hand, hematite,  $\text{Fe}_2\text{O}_3$ , has never been observed under these conditions. There seems to be a barrier to its formation, though it is a common product of oxidation when the contact with oxygen is continuous and unrestricted and time is allowed for the reaction to approach equilibrium.

As an example of the former conditions may be quoted the process of dry wear of iron and steels which has been studied by X-rays<sup>(1)</sup> and yielded the result that the abraded powdery products of wear consisted of  $\alpha$ -iron,  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  in various proportions, but not  $\text{Fe}_2\text{O}_3$ . Under the heading "limited accessibility of oxygen" can also be considered the products of corrosion of steel in close contact with the metal, which are to some degree "protected" by the outer layers of scale; on iron exposed to the atmosphere at  $1000^\circ\text{C}$ . the innermost layer of scale was found to be pure wüstite.

The object of the following considerations is to show that the structures of the phases  $\alpha$ -Fe,  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  have not merely the common feature of cubic symmetry, but that simple quantitative relations exist which facilitate a ready transition between the phases, by relatively small atomic readjustments.  $\text{Fe}_2\text{O}_3$ , on the other hand, has a fundamentally different crystal structure (rhombohedral, corundum type), and the energy barrier to its formation from the cubic phases will be greater than is the case during the transformations:



For reference, the iron-oxygen equilibrium diagram is shown in Fig. 1 as given by Hansen.<sup>(2)</sup> While considerable uncertainty still attaches to the part  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$ , the liquidus curves and the accurate phase boundaries of wüstite, the general characteristics of the phase fields in the part  $\text{Fe}$ - $\text{FeO}$ - $\text{Fe}_3\text{O}_4$  may be regarded as established, in particular the eutectoid transformation  $4\text{FeO} \rightleftharpoons \text{Fe} + \text{Fe}_3\text{O}_4$  at  $570^\circ\text{C}$ . A diagram showing phase boundaries determined by various workers, as well as numerous references, may be found in the paper by Pfeil and Winterbottom.<sup>(3)</sup>

## (2) THE DIMENSIONS OF THE UNIT CELLS OF $\alpha$ -Fe, $\text{FeO}$ AND $\text{Fe}_3\text{O}_4$ .

The three phases  $\alpha$ -Fe,  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  have the body-centred cubic, the sodium chloride and the spinel type of structure, respectively. The sides of the unit cells are as follows:

Phase . . . . .	$\alpha$ -Fe.	$\text{FeO}$ .	$\text{Fe}_3\text{O}_4$ .
Lattice spacing ( $a$ ) . . . . .	2.861 Å.	4.290 Å.*	8.41 Å.†

\* Value at eutectoid composition of wüstite; regarding spacing variations, see later.

† According to Glocker.<sup>(4)</sup> The value 8.37 Å. quoted by Wyckoff<sup>(5)</sup> is probably too low, owing to solid solution of other elements. Bragg,<sup>(6)</sup> quoting Holgersson,<sup>(7)</sup> gives 8.42 Å.

The ratios of these values are :

$$\begin{aligned} a_{\text{FeO}} : a_{\text{Fe}} &\approx 1.50, & a_{\text{Fe}_3\text{O}_4} : a_{\text{FeO}} &\approx 2 \text{ (actually 1.96).} \\ a_{\text{Fe}_3\text{O}_4} : a_{\text{Fe}} &\approx 3 \text{ (actually 2.94).} \end{aligned}$$

Therefore it is virtually :

$$a_{\text{Fe}} : a_{\text{FeO}} : a_{\text{Fe}_3\text{O}_4} = 1 : 1.5 : 3 \text{ or } \frac{1}{3} : \frac{1}{2} : 1.$$

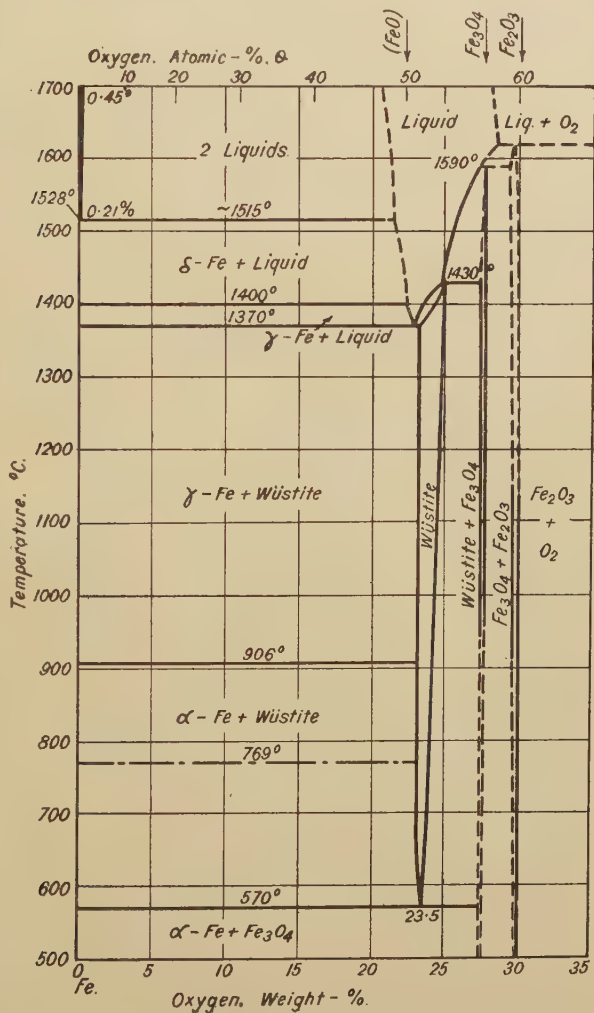


FIG. 1.—Iron-Oxygen System, according to Hansen.<sup>(2)</sup>

This is also brought out in Fig. 2, where the actual and relative values of the edges of the three unit cells are shown. This interconnection by simple ratios makes it possible to represent a whole number of unit cells within the same volume, *viz.*, one of  $\text{Fe}_3\text{O}_4$ ,

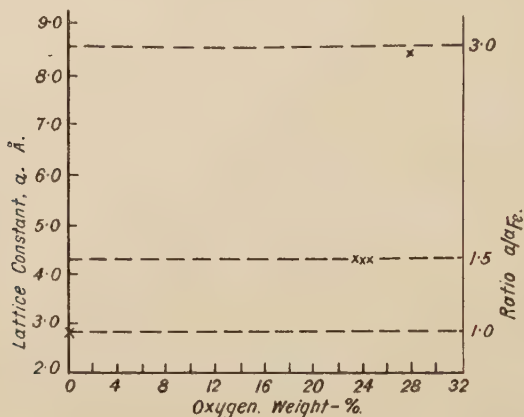


FIG. 2.—Absolute and Relative Lattice Constants of  $\alpha$ -Fe, Wüstite and  $\text{Fe}_3\text{O}_4$ .

$2^3$  of  $\text{FeO}$  and  $3^3$  of  $\alpha$ -Fe. This has been done in Fig. 3(a), (b), (c), which shows one unit cell of the spinel structure ( $\text{Fe}_3\text{O}_4$ ) and, drawn to the same scale, 8 of  $\text{FeO}$  and 27 of  $\alpha$ -iron.

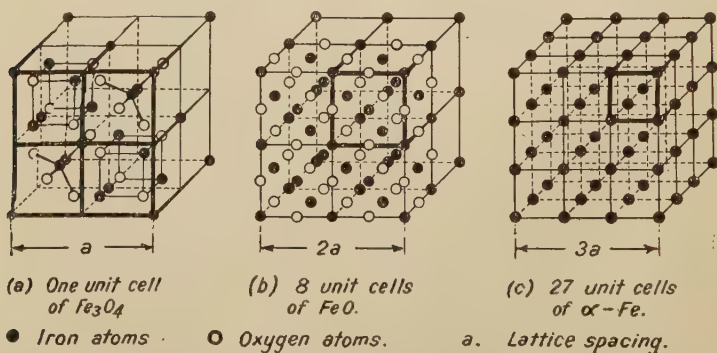


FIG. 3.—Pseudo-Unit Cells of  $\alpha$ -Fe,  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ . (The back layers in the drawing have not been filled in for the sake of clarity.)

On comparing these three "pseudo"-unit cells, it can be seen that the atomic rearrangements necessary to pass from one structure to the other, bound up with the insertion of oxygen and the removal

of iron atoms, can be achieved by certain operations within the framework of the same cube. It is believed, therefore, that the physical transformation from one phase to the other, such as occurs during short-time oxidation, is able to proceed without fundamental disturbance and with comparative ease, and possibly even to stop at intermediate stages. (Anticipating the results of a later discussion, the whole wüstite solubility range may be regarded as such an intermediate stage between ideal FeO and Fe<sub>3</sub>O<sub>4</sub>.) On the other hand, rhombohedral Fe<sub>2</sub>O<sub>3</sub>, which chemically differs from Fe<sub>3</sub>O<sub>4</sub> by only 2.9 atomic-% of oxygen, corresponds to an entirely different atomic arrangement. It is, therefore, significant that in the instance of the wear products, Fe<sub>2</sub>O<sub>3</sub> is absent and the constitution is confined to the three phases of the cubic type. In order to initiate the transformations Fe → FeO → Fe<sub>3</sub>O<sub>4</sub> a considerably lower energy barrier will have to be overcome than in forming rhombohedral Fe<sub>2</sub>O<sub>3</sub> from Fe<sub>3</sub>O<sub>4</sub>. Therefore, assuming otherwise equal experimental conditions, the temperature necessary to bring about this last stage will be appreciably higher than that required for the first two stages. It would follow that during dry wear this higher temperature had not been reached.

The number of atoms within the three pseudo-unit cells of α-Fe, FeO and Fe<sub>3</sub>O<sub>4</sub> (Fig. 3) is given in Table I.

TABLE I.—*Number of Atoms in Pseudo-Unit Cells.*

Phase.	Number of Atoms per Pseudo-Unit Cell.		
	Total.	Iron.	Oxygen.
Fe <sub>3</sub> O <sub>4</sub> . . .	56	24	32
FeO . . .	64 (= 8 × 2 <sup>3</sup> )	32	32
α-Fe . . .	54 (= 2 × 3 <sup>3</sup> )	54	0

Among the three phases, FeO has the most closely packed structure; this is already implied by its sodium chloride type of lattice. Therefore, an enclosed system (α-iron crystal + oxygen) suffers contraction when forming FeO, and a slight contraction when forming Fe<sub>3</sub>O<sub>4</sub>; an enclosed system (FeO crystal + oxygen), on the other hand, expands when forming Fe<sub>3</sub>O<sub>4</sub>. This expansion is to a small extent countered by the lattice contraction occurring within the wüstite solid solution on adding oxygen.

Table I. shows, further, that, while the transition from Fe to FeO obviously increases the number of bound oxygen atoms within a given volume, this number remains constant during the second stage, FeO → Fe<sub>3</sub>O<sub>4</sub>. In a sense, therefore, the first stage involves a true "oxidation," but the second stage does not, if by this term we mean a gain of oxygen atoms per unit volume. α-Fe forms FeO

or  $\text{Fe}_3\text{O}_4$  by a gain of oxygen and a loss of iron atoms, while  $\text{FeO}$  forms  $\text{Fe}_3\text{O}_4$  by a loss of iron atoms only.

Considering the three pseudo-unit cells in Fig. 3, the relation between  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  is founded on a definite mechanism of atomic movements to be discussed. The transition from  $\alpha$ -iron to the two oxides would involve more complex atomic displacements within the frame of the outer cube; the eight corner atoms defining this cube are the only ones to maintain their positions. The simple spacing ratio should, for the present purpose, be considered merely as an empirical fact, of which use will be made.

Besides the rhombohedral (or low-temperature  $\alpha$ ) form of  $\text{Fe}_2\text{O}_3$ , there also exists a cubic high-temperature modification of this compound ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ), having the spinel type of structure.<sup>(8)</sup> The difference from  $\text{Fe}_3\text{O}_4$  consists in the random omission of cations from the unit cell, while the number of oxygen ions remains constant (32 oxygen ions in both,  $21\frac{1}{3}$  iron ions in  $\gamma$ - $\text{Fe}_2\text{O}_3$ , as against 24 in  $\text{Fe}_3\text{O}_4$ ). The mode of formation of  $\gamma$ - $\text{Fe}_2\text{O}_3$  from  $\text{Fe}_3\text{O}_4$  could be discussed on similar lines to those outlined for the other phase transitions in this paper.

### (3) THE VARIATION OF LATTICE DIMENSIONS WITHIN THE WÜSTITE SOLID SOLUTION. COMPARISON WITH $\alpha$ -Fe AND $\text{Fe}_3\text{O}_4$ .

Wüstite ( $\text{FeO}$ ) possesses a certain solubility for oxygen, causing the lattice dimensions to change. The value of 4.290 Å. used above corresponds to the eutectoid composition.

According to Jette and Foote's X-ray investigation,<sup>(9, 10)</sup> an increase of iron content expands the wüstite lattice. The spacings vary linearly with composition (see diagram in their paper<sup>(9)</sup>). The values, given by these authors, range from 4.3023 Å. at the iron-rich side of the solubility region to 4.272 Å. at the less accurately determined oxygen-rich side. The corresponding compositions are:

Saturation in Fe: 23.21 weight-%, i.e., 51.34 atomic-% of oxygen.  
Saturation in  $\text{O}_2$ : 24.28 weight-%, i.e., 52.91 atomic-% of oxygen.

The eutectoid composition of wüstite is:

23.60 weight-%, i.e., 51.87 atomic-% of oxygen.

The whole solubility range thus lies on the high-oxygen side of the ideal composition " $\text{FeO}$ ." But different workers disagree as to whether or not at very high temperatures the true compound may not exist (Andrew, Maddocks and Howat,<sup>(11)</sup> and Schenck and Hengler<sup>(12)</sup> claim to have preserved it in a metastable state).

The lattice spacings will be referred to as follows:

Wüstite at the iron side of the solid solution:	$a_{\text{FeO}}^+$	(= 4.302 Å.)
Wüstite at the eutectoid composition:	$a_{\text{FeO}}^E$	(= 4.290 Å.)
Wüstite at the $\text{Fe}_3\text{O}_4$ side of the solid solution:	$a_{\text{FeO}}^-$	(= 4.272 Å.)
$\alpha$ -iron:	$a_{\text{Fe}}$	(= 2.861 Å.)
Magnetite:	$a_{\text{Fe}_3\text{O}_4}$	(= 8.41 Å.)



Then the ratios of lattice spacings for different wüstite compositions, in elaboration of the values stated in Section 2, become :

$$\left. \begin{aligned} a_{\text{FeO}}^+ : a_{\text{Fe}} &= 1.503 \\ a_{\text{FeO}}^E : a_{\text{Fe}} &= 1.499 \\ a_{\text{FeO}}^- : a_{\text{Fe}} &= 1.493 \end{aligned} \right\} \begin{array}{l} i.e., \\ 3 : 2 \\ \text{approx.} \end{array} \quad \left. \begin{aligned} a_{\text{Fe}_3\text{O}_4} : a_{\text{FeO}}^+ &= 1.955 \\ a_{\text{Fe}_3\text{O}_4} : a_{\text{FeO}}^E &= 1.960 \\ a_{\text{Fe}_3\text{O}_4} : a_{\text{FeO}}^- &= 1.969 \end{aligned} \right\} \begin{array}{l} i.e., \\ 2 : 1 \\ \text{approx.} \end{array}$$

These figures reveal several facts :

(1) The simple ratio relation essentially still applies, being only slightly modulated by the solid solubility in wüstite. This subsidiary variation is, however, of significance.

(2) The maximum deviation of the ratio  $a_{\text{FeO}} : a_{\text{Fe}}$  from the 3 : 2 value is 0.6% and occurs for the composition of wüstite farthest from the iron side ( $a_{\text{FeO}}^-$ ).

(3) Comparing the wüstite with the Fe<sub>3</sub>O<sub>4</sub> spacings, the ratio of 2 : 1 is approached with increasing oxygen content of the wüstite lattice. The solubility, however, breaks down before the exact value of the ratio is reached. The maximum deviation is 2% and occurs on the iron side of the wüstite range.

The results can best be shown graphically. For this purpose the values of the lattice spacings of the three phases have been reduced to the same scale, namely, that of  $\alpha$ -iron, by taking  $\frac{2}{3}$  of the actual wüstite spacing and  $\frac{1}{3}$  of that of Fe<sub>3</sub>O<sub>4</sub>. (The reason for this procedure arises out of the relations established earlier and shown once more at a glance in Fig. 2. By rendering the spacings thus arithmetically comparable, it is possible to discuss the further question of systematic deviations from the exact ratio.) The reduced values of the oxide spacings are as follows :

$$\begin{aligned} \frac{2}{3} a_{\text{FeO}}^+ &= 2.868 \text{ \AA. (Wüstite at iron-rich boundary).} \\ \frac{2}{3} a_{\text{FeO}}^E &= 2.860 \text{ \AA. (Wüstite at eutectoid composition).} \\ \frac{2}{3} a_{\text{FeO}}^- &= 2.848 \text{ \AA. (Wüstite at oxygen-rich boundary).} \\ \frac{1}{3} a_{\text{Fe}_3\text{O}_4} &= 2.803 \text{ \AA. (Magnetite).} \end{aligned}$$

In Fig. 4 these values have been plotted against composition. Within the wüstite solubility range the spacings change linearly, in accordance with the work of Jette and Foote, but it can be seen further that, on extrapolating to higher oxygen contents, the Fe<sub>3</sub>O<sub>4</sub> value falls on to the same straight line. It is believed that this last result is new.

It indicates that the fundamental relation between the FeO and Fe<sub>3</sub>O<sub>4</sub> structures is an even closer one than was presumed earlier. Starting from the ideal composition FeO of fully occupied lattice points, the wüstite lattice loses iron atoms, until the sodium chloride type of structure becomes unstable (solid-solution boundary). With more oxygen an atomic rearrangement takes place (change to Fe<sub>3</sub>O<sub>4</sub>), which, however, does not alter the cubic symmetry and the basic framework of the structure. The structural relationship is found

now to be even so close that the linear decrease of lattice constants with the addition of oxygen, associated in the first place with the

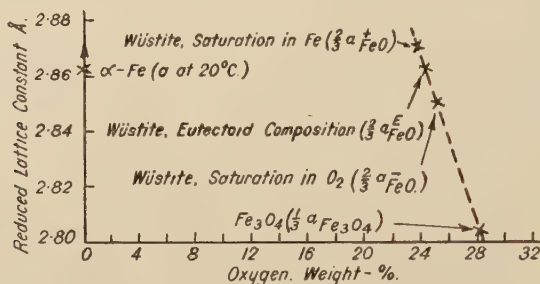


FIG. 4.—Lattice Constants, reduced to the scale of that of  $\alpha$ -Fe, as a function of the oxygen content.

wüstite solid solution, though interrupted by the two-phase field, extends to the Fe<sub>3</sub>O<sub>4</sub> phase as though the change in lattice structure had been of no influence.

#### (4) DISCUSSION OF THE TRANSITION $FeO \rightarrow Fe_3O_4$ .

In the ideal FeO structure the  $Fe^{++}$  and  $O^{--}$  ions each form a set of interlacing face-centred cubic lattices. Since, however, the wüstite range lies wholly on the oxygen side of the composition FeO, certain  $Fe^{++}$  ion positions, distributed at random, have to be considered vacant, their number increasing as solid solution proceeds. In alloy solid solutions omission of atoms from lattice points without alteration of the structure is a well-known occurrence (e.g., nickel-aluminium, Bradley and Taylor<sup>(13)</sup>; Lipson and Taylor<sup>(14)</sup>). A similar phenomenon may well occur in the case of the ionic bond, and the wüstite lattice in particular, provided that compensation of the electric charge takes place. The radii of the ions concerned are, according to Bragg<sup>(6)</sup> (*loc. cit.*, p. 31)  $Fe^{++} = 0.83 \text{ \AA.}$ ,  $O^{--} = 1.32 \text{ \AA.}$ ,  $Fe^{+++} = 0.67 \text{ \AA.}$  The assumption that in the wüstite lattice the excess oxygen ions replace those of iron therefore cannot be reconciled with the observed decrease of lattice constant with decreasing iron content. Substitutional replacement by the larger oxygen ions would, on the contrary, expand the lattice. However, the decrease of lattice constant can be explained by assuming that during solid solution the  $Fe^{++}$  positions in the original lattice are in part filled by the smaller  $Fe^{+++}$  ions and in part remain vacant. This can still be interpreted as "substitution" of divalent iron by trivalent iron plus "holes." The maintenance of electronic equilibrium imposes the condition that for every one  $Fe^{++}$  ion dropped from the lattice two others are ionised to  $Fe^{+++}$ . This would not only explain the decrease in lattice constant but also provide the continuity to Fe<sub>3</sub>O<sub>4</sub>,

which may be regarded as the final stage of this process of replacement, since  $\text{Fe}_3\text{O}_4 = \text{Fe}^{++}\text{O} \cdot \text{Fe}_2^{+++}\text{O}_3$ . The changes within the wüstite lattice during solid solution thus only involve the metallic sites and leave those of the oxygen ions unaffected, *i.e.*, during this "oxidation" the number of oxygen ions within a given lattice volume does not increase, merely that of iron ions decreases. This falls into line with the earlier observation that the number of oxygen ions per pseudo-unit cell is the same (32) in both the ideal FeO and the  $\text{Fe}_3\text{O}_4$  lattices, while that of iron ions decreases (from 32 to 24).

The replacement of ferrous ions by ferric ones and by "holes" would in general cause a linear change in lattice constant (known as "Vegard's law" in alloy structures), unless anomalies occur, such as superlattice formation. Since such a linear decrease within the wüstite region is actually observed, it can reversely be concluded that the replacement occurs in a random manner.

The apparent extension of Vegard's law to include the  $\text{Fe}_3\text{O}_4$  lattice (Fig. 4) provides further evidence for the manner of atomic rearrangement during the transition wüstite  $\rightarrow$  magnetite. A study of Figs. 3(a) and 3(b) shows that structurally the iron ions can be divided into two classes:

*A.*—Those forming the gross face-centred cubic skeleton of the  $\text{Fe}_3\text{O}_4$  unit cell (*see* Fig. 3(a)); this repeats itself in Fig. 3(b).

*B.*—The remaining iron atoms which, together with those of oxygen, occupy different positions in the two lattices.

The group *B* ions, while in wüstite occupying the main (100) planes, take up in  $\text{Fe}_3\text{O}_4$  positions inside the unit cell, *i.e.*, inside the cube of *A* ions. This can be interpreted by saying that as solid solution in wüstite proceeds and the  $\text{Fe}^{++}$  ions are gradually replaced by  $\text{Fe}^{+++}$  and by holes, the iron lattice *A* contracts progressively, until from a certain stage onwards it is no longer possible for the large oxygen ions to be accommodated in their original lattice positions; they are then displaced to interior positions together with the iron ions other than *A*.

It may well be that in  $\text{Fe}_3\text{O}_4$  the structural distinction between the *A* and *B* types of iron ions coincides with the electrostatic one between  $\text{Fe}^{+++}$  and  $\text{Fe}^{++}$  ions. It would appear that group *A* agrees with  $\text{Fe}^{++}$  and group *B* with  $\text{Fe}^{+++}$ , because it is the *A* lattice in wüstite which maintains its identity in  $\text{Fe}_3\text{O}_4$ . This is supported quantitatively, with a certain modification, by the following consideration: Among the twenty-four iron ions of the  $\text{Fe}_3\text{O}_4$  unit cell (Fig. 3(a)), twenty occupy inside positions *B*, and four outside ones *A*. (Note: In counting, it must be borne in mind that the *A* ions are shared with the adjoining unit cells, while all the *B* ions belong to the given cell.) In  $\text{Fe}_3\text{O}_4$  the ferric ions should be in a majority of 2:1. Writing  $\text{Fe}_8\text{O}_8 \cdot \text{Fe}_{16}\text{O}_{24}$ , in conformity with the total number of 56 atoms per unit cell, there would be 8  $\text{Fe}^{++}$  and 16  $\text{Fe}^{+++}$  ions. Structurally the *B* positions can be subdivided into

two classes, easily recognised in Fig. 3(a), if the eight cubic sectors of the unit cell are considered separately: Four iron ions occupy the centres of four of these sectors (class  $B_1$ ) and sixteen are found in the other four, forming a set of four within each sector (class  $B_2$ ). Thus there exist in the magnetite cell:

8  $\text{Fe}^{++}$  ions and 16  $\text{Fe}^{+++}$  ions,  
also 4  $A$  sites, 4  $B_1$  sites and 16  $B_2$  sites.

Therefore, assuming that the  $\text{Fe}^{++}$  ions occupy the  $A + B_1$  positions and the  $\text{Fe}^{+++}$  ions the  $B_2$  ones, the numerical agreement between the electronic and the structural division would be exact. This distribution of ions is most probable and would agree with the known spinel structure. A description of the spinel type of structure in general has been given by Sir Lawrence Bragg<sup>(6)</sup> (*loc. cit.*, p. 97). The "set  $B_1$ " of metal ions would correspond to four-co-ordination between a tetrahedral group of oxygen ions, the set  $B_2$  to six-co-ordination between an octahedral group. This again emphasises the divalent and trivalent nature, respectively, of the groups of iron ions, which would follow from the distribution suggested above.

The straight-line relation between the lattice constants of wüstite and  $\text{Fe}_3\text{O}_4$  (Fig. 4) can, therefore, be taken as a consequence of the continued identity of the  $A$  lattices in both phases. The only changing factor is the random omission of iron atoms under readjustment of the valency of the remaining ones. Normally a discontinuity in the linear relation of spacings would be expected during the change-over to the  $\text{Fe}_3\text{O}_4$  phase, but the ionic readjustment appears to be such as to cause the least possible disturbance to this continuity. A very slight deviation from the straight line, caused by the structural change, is, of course, possible, but would be within the accuracy of the available data.

The above theory of atomic replacement within the wüstite range in part agrees with Jette and Foote's own interpretation of their results,<sup>(9, 10)</sup> but more satisfactorily with Hägg's comment.<sup>(15)</sup> Jette and Foote assumed a complex form of substitution, in which "an oxygen ion replaces an  $\text{FeO}$  group." This contention is criticised by Hägg, who quotes the quite similar case of ferrous sulphide,<sup>(16)</sup> showing that when  $\text{FeS}$  contains more sulphur than corresponds to the formula this excess is caused by vacant points in the iron lattice. Vacant lattice positions in ionic compounds render possible a new type of phase with variable composition, which Hägg terms "subtraction" type. Accordingly wüstite would be a subtraction type of solid solution in  $\text{FeO}$ .

The existence of this type seems to be very important from another aspect. The vacant positions open the possibility of  $\text{FeO}$  readily taking into solid solution all kinds of elements with which it may be in contact, if their ions are of suitable size and valency, such as  $\text{Mg}^{++}$  from  $\text{MgO}$ .

The above results have been obtained purely on grounds of atomic



structure, but a brief explanation of their chemical meaning seems necessary. If the iron-richest member of the wüstite series "oxidises" it does not, according to the above, gain oxygen but loses ferrous iron in favour of a smaller amount of ferric iron. This refers only to a given volume within the wüstite crystals, as otherwise it would contradict the actual chemical gain in weight due to the absorption of oxygen. During actual oxidation the iron expelled from the primary lattice combines with the added oxygen to form new wüstite unit cells assembling around the original ones.

# (5) EXPERIMENTAL EVIDENCE FOR THE CONTRACTION OF THE WÜSTITE LATTICE.

All the above considerations depend on the fact that the wüstite lattice contracts with increasing oxygen content, and does not expand or remain constant as suggested by earlier workers.<sup>(17, 18)</sup> The lattice contraction has been verified by certain experiments of

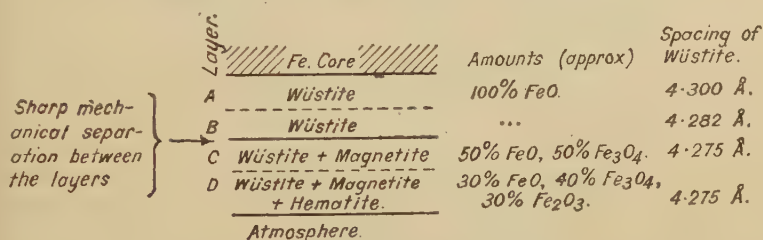


FIG. 5.—Phase Constitution and Wüstite Spacings of Layers of Scale Formed on Pure Iron at 1000° C.

the author, in which the scale formed on iron and steels at high temperatures was examined.

When pure iron (Hilger) was exposed to the atmosphere at 1000° C. and rapidly cooled, distinct and easily separable layers of scale were formed. Each of these layers was subjected to X-ray examination.

The layer of oxide in direct contact with the iron core was found to be pure wüstite, the adjoining outer layers containing increasing amounts of Fe<sub>3</sub>O<sub>4</sub>, while in the outermost layer Fe<sub>2</sub>O<sub>3</sub> appeared as an additional phase. This sequence of phases has already been demonstrated by microscopical and chemical methods in Pfeil's work.<sup>(19)</sup> Wüstite was present in all the layers; its lattice spacing markedly decreased with the distance from the iron core. The spacing values and the phase constitutions of the respective layers are shown diagrammatically in Fig. 5.



The approximate dimensions of the rod and layers in this experiment were as follows :

Before test :	Metal rod	$\approx 5$ mm. dia.
After test :	Total thickness with scale	$\approx 7.5$ mm. dia.
	Metal core	$\approx 2.8$ mm. dia.
(Inner)	Layer <i>A</i>	$\approx 0.25$ mm. thick.
	Layer <i>B</i>	$\approx 0.15$ mm. thick.
	Layer <i>C</i>	$\approx 0.75$ mm. thick.
(Outer)	Layer <i>D</i>	$\approx 1.2$ mm. thick.

The outer layer was of a smooth, velvety appearance and, together with layer *C*, formed a thick hard shell around the core plus inner layers. The general character of the layers persisted over a wide range of temperatures lower than  $1000^{\circ}\text{C.}$ , though their relative and absolute dimensions varied considerably.

These results illustrate concisely many features of the iron-oxygen system. But the point to be emphasised here is the evident decrease of spacing with distance from the metal core. Layers *A* and *B*, according to their spacing, correspond to different compositions within the wüstite solid solution. The value  $4.300 \text{ \AA.}$  for layer *A* agrees well with that given by Jette and Foote's near wüstite saturated in iron. Using Jette and Foote's curve of lattice constants as a "calibration curve" for composition, it would follow that layer *A* corresponds to 23.25% of oxygen. The spacing value for layers *C* and *D* is near that given by Jette and Foote for oxygen saturation of the wüstite region and would correspond to 24.2% of oxygen by weight. The constancy of spacing in layers *C* and *D* also indicates that this wüstite corresponds to a phase-boundary composition. According to the phase rule this should be so, as in these layers wüstite co-exists with other, oxygen-richer, phases. (But as we cannot assume equilibrium conditions, a difference in spacing might have been possible.)

Incidentally, the use of X-ray analysis to determine the oxygen content in a given mass of iron oxide seems to be a method worth considering. Provided that the basic data have once been reliably ascertained, lattice-spacing curves and proportions of the oxide phases could be correlated.

#### (6) $\gamma$ -IRON IN RELATION TO WÜSTITE AND MAGNETITE.

The question arises in which way the crystal structures of wüstite and  $\gamma$ -iron are related. They have the common feature of being stable at high temperatures only ( $\gamma$ -Fe above  $906^{\circ}\text{C.}$ , wüstite above  $570^{\circ}\text{C.}$ ). Also, according to Schenck and Hengler,<sup>(12)</sup> the solubility of oxygen is probably somewhat higher in  $\gamma$ -Fe than in  $\alpha$ -Fe, though this has not been fully proved.

The lattice of  $\gamma$ -iron is face-centred cubic, and so is that of the iron atoms in FeO (Fig. 3(b)). In fact, if the ionisation of the iron atoms is taken into account, the FeO lattice may plainly be con-

sidered as that of  $\gamma$ -Fe widened by the insertion of oxygen ions, with a simultaneous decrease of the radius of the metal atom corresponding to the difference in size between the neutral Fe atom and the Fe<sup>++</sup> ion. This can be readily verified by calculation, using the known values for the atomic diameters.

The lattice spacings of  $\gamma$ -iron are, according to Wyckoff <sup>(5)</sup> (*loc. cit.*, p. 205), 3.63 Å. at 1100° C. and 3.68 Å. at 1425° C.; extrapolation to room temperature gives 3.56<sub>4</sub> Å. (quoted by Hume-Rothery <sup>(20)</sup>) and to 900° C. (*i.e.*, near the A<sub>3</sub> point) 3.60 Å.

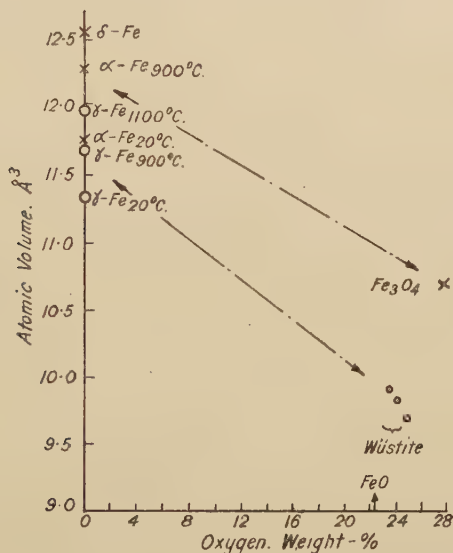


FIG. 6.—Atomic Volumes of  $\alpha$ -Fe,  $\gamma$ -Fe, Wüstite and Fe<sub>3</sub>O<sub>4</sub>.

As the number of atoms per unit cell ( $N$ ) is 2 in  $\alpha$ -Fe and 4 in  $\gamma$ -Fe, it is advisable to compare atomic volumes ( $V$ ) rather than lattice constants ( $a$ ). The results of the corresponding calculations are shown in Fig. 6, and may briefly be stated as follows :

(1) Within the wüstite range the atomic volumes increase with increasing iron content and approach those of the  $\alpha$  and  $\gamma$  forms of pure iron.

(2) Considering equivalent temperatures (*e.g.*, 20° C. or 900° C.), the ratios  $V(\text{oxide})/V(\text{Fe})$  are throughout nearer unity if  $\gamma$ -iron instead of  $\alpha$ -iron is chosen as a base.

(3) The atomic volume of Fe<sub>3</sub>O<sub>4</sub> is higher than those of wüstite, owing to the less dense atomic packing in spinel (*cf.* Table I.), so that it again approaches that of pure iron.

The close structural relation between  $\gamma$ -iron and wüstite mentioned, which consists in the Fe atoms occupying the same face-centred cubic lattice in both phases, may now be elaborated by a glance at Fig. 6. It reveals a pronounced parallelism between the relative atomic volumes of  $\gamma$ -Fe and wüstite on the one hand and  $\alpha$ -Fe and  $\text{Fe}_3\text{O}_4$  on the other. The expansion associated with the  $\gamma$ - $\alpha$  change seems to be simulated by that occurring during the transformation wüstite  $\rightarrow \text{Fe}_3\text{O}_4$ . The change from  $\gamma$ - to  $\alpha$ -iron is determined by temperature only, the change from FeO to  $\text{Fe}_3\text{O}_4$  by composition as well as temperature (eutectoid decomposition). The association of  $\gamma$ -iron with wüstite and of  $\alpha$ -iron with magnetite, based on the relation of their atomic volumes, is also borne out by a study of the iron-oxygen diagram (Fig. 1).  $\text{Fe}_3\text{O}_4$  is stable at all temperatures up to its melting point, and so is body-centred cubic iron, except for the interruption at the  $\gamma$ -iron range. From the structural point of view, the iron-oxygen system may be likened to one having "a closed  $\gamma$ -loop," although in this case it is not a question of solid solutions but of the formation of new structures of a related type.

It may be remarked that FeO and austenite are both non-magnetic, in contrast to  $\text{Fe}_3\text{O}_4$  and ferrite.

An attempt has been made to obtain experimental support for these relations, and some preliminary results will be reported in the following Section.

#### (7) THE $\gamma$ - $\alpha$ CHANGE AND THE OXIDES; EXPERIMENTS AND FURTHER DISCUSSION.

The tests were on the same lines as those reported in Section 5. The idea was to see whether it made any difference to the phase constitution of the innermost layer of scale, whether the temperature of exposure was just below or just above the  $A_3$  point. Clean pieces of pure iron (Hilger) were again allowed to oxidise in the atmosphere. The temperatures were  $1000^\circ$ ,  $920^\circ$  and  $890^\circ \text{C.}$ , *i.e.*,  $\pm 15^\circ$  around  $A_3$ , and  $850^\circ \text{C.}$  Several sharply defined layers of scale could again be distinguished; the outer layer *D* (see Fig. 5) formed a hard shell, with layer *C* loosely adhering at its inside, and surrounding the core with layers *A* and *B*. The present emphasis is laid on the oxide *A* in direct contact with the iron core, but for interest the layers *D* were also examined, for three temperatures.

The results are summarised in Table II. The conclusions can be stated as follows.

##### *Inner Layer.*

(1) Wüstite was always the predominant oxide, as was to be expected at temperatures above  $570^\circ \text{C.}$

(2) Wüstite was the only oxide present at  $1000^\circ$  and  $920^\circ \text{C.}$ ,

while at 890° C. it was accompanied by a small amount of Fe<sub>3</sub>O<sub>4</sub>, and at 850° C. by a considerable amount of this phase. The estimated quantities are given in the Table, with the proviso that traces of any phases below the X-ray visibility limit cannot of course be included. (Note: Some metallic iron from the core was noted in two of the samples, which was introduced during the removal of the innermost layer of scale from the metal with the aid of a file; its presence was clearly incidental, and can reasonably be disregarded.)

Thus, above the A<sub>3</sub> point (906° C.), we have FeO only, below it FeO with Fe<sub>3</sub>O<sub>4</sub> in increasing proportions. This is stated as an empirical observation, and is not put forward as a conclusive proof for a causal connection between the  $\alpha$ - $\gamma$  transformation and the

TABLE II.—Oxide Layers Formed on Pure Iron at Temperatures around A<sub>3</sub>.

Layer.	850° C.	890° C.	920° C.	1000° C.
(a) Phase Constitution of Oxides. (Approximate molecular percentage in brackets.)				
Inner Layer A .	FeO + Fe <sub>3</sub> O <sub>4</sub> (60) (40)	FeO + small Fe <sub>3</sub> O <sub>4</sub> (85) (15)	FeO, no Fe <sub>3</sub> O <sub>4</sub> (100)	FeO, no Fe <sub>3</sub> O <sub>4</sub> (100)
Outer Layer D .	...	FeO + Fe <sub>3</sub> O <sub>4</sub> (80) (35) + trace Fe <sub>3</sub> O <sub>3</sub> (5)	FeO + Fe <sub>3</sub> O <sub>4</sub> (30) (40) + Fe <sub>3</sub> O <sub>3</sub> (30)	FeO + Fe <sub>3</sub> O <sub>4</sub> (30) (40) + Fe <sub>3</sub> O <sub>3</sub> (30)
(b) Lattice Constants of Wüstite. Å.				
Inner Layer A .	4.284	4.298	4.299	4.300
Outer Layer D .	...	4.276	4.278	4.275

phase constitution of the scale. However, the suggestion of such a connection is strong and would be in harmony with the above theory. The layer of pure FeO formed above A<sub>3</sub> (i.e., in contact with  $\gamma$ -iron) may be considered to be derived from the original metal lattice, with the oxygen ions inserted in their appropriate positions. On quenching from temperatures below A<sub>3</sub>, this lattice continuity between metal and ferrous oxide will disappear, and the tendency of the FeO lattice to decompose increases with decreasing temperature, and at 570° C. and below this process is complete.

Fig. 7 shows the approximate amounts of FeO and Fe<sub>3</sub>O<sub>4</sub> in the inner layer of scale (Table II.) plotted against temperature. It can be seen that on tentatively extrapolating the curve indicated by the 850° and 890° C. points, it intersects the 100% FeO horizontal just above 900° C., i.e., around the A<sub>3</sub> point. However, more experimental points will be required before any such connection can be fully established.

(3) The lattice-spacing values of wüstite (in the layers A) are nearly constant for 1000°, 920° and 890° C., though slightly decreasing, while a considerable fall occurs for the 850° C. sample. The

values cannot readily be correlated with the oxygen content, as was possible in the case of different layers of the same specimen, since temperature introduces another variable. But the lower value (4.284 Å.) for 850° C. would indicate a wüstite composition richer in oxygen than that corresponding to higher temperatures; this would agree with the observed co-existence in this sample of appreciable amounts of  $\text{Fe}_3\text{O}_4$ .

#### Outer Layer.

In the outer layers of scale (*D*) wüstite has in all cases a considerably smaller lattice constant than in the inner ones (*A*), clearly showing the higher oxygen content.

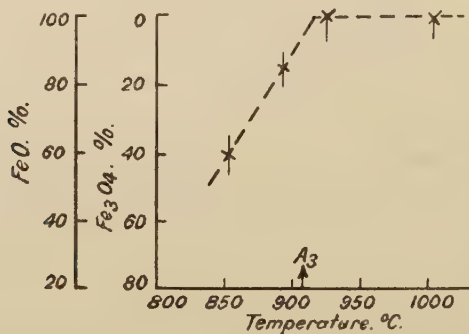


FIG. 7.—Phase Constitution of Inner Layers of Scale Formed on Pure Iron at Various Temperatures.

The phase constitution of the outer layers (Table II.) is such that at 1000° and 920° C. the relative amounts of  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  are unchanged, namely, 30%, 40% and 30%. However, at 890° C.  $\text{Fe}_2\text{O}_3$  has fallen to a trace and  $\text{Fe}_3\text{O}_4$  has slightly decreased, both in favour of  $\text{FeO}$ , which has risen to 60%. That is, the total oxygen content of the oxides in bulk has undergone the corresponding decrease. Comparing this with the inner layers (Table II.), it appears that below the  $A_3$  point an outward migration of iron atoms has taken place; on the other hand, within the  $\gamma$  region the constitutions of both layers do not differ at the two temperatures, *i.e.*, such migration between layers is inhibited, according to the above, by the structural affinity and mechanical continuity of the  $\gamma$ -iron and wüstite lattices.

From this point of view, wüstite on top of austenite is equivalent to a protective coating, provided that no lattice disruption takes place. It is thus suggested that the properties of austenitic heat-resisting steels may be explained in part on the basis of this continuity of structure, although added elements (nickel, chromium,



silicon, &c.) introduce other factors of predominant influence. But, the question arises whether for equal composition the face-centred cubic structure is not inherently more scaling-resistant than the body-centred one. Generally the attempt seems worth while to apply (1) the structure relationships between oxides and base metal and (2) the principle of vacant lattice points to the problem of the corrosion resistance of steels.

In discussions on scaling, FeO and  $\text{Fe}_3\text{O}_4$  have frequently been regarded as unrelated phases. It has also been assumed that a disruption of the oxide layer follows from a transformation from one phase to the other, leading to further oxidation of the base metal. According to the present theory this is not bound to happen. Segregation of crystallites of  $\text{Fe}_3\text{O}_4$  from primary FeO may well take place without causing a physical disruption, or such disruption may be minimised through the continued identity of the group A ion lattice in both structures. In practice, the maintenance of this crystal continuity can be aided by the addition of certain alloying elements (*e.g.*, nickel, chromium) going into solid solution in the sodium chloride and spinel structures. Their task would essentially be to modify the number of vacant cation positions in the wüstite lattice and to eliminate abrupt changes in atomic volume during the change to magnetite.

Electron-diffraction studies on thin oxide films, such as have recently been carried out by Quarrell,<sup>(21)</sup> deal with layers of a much lower order of magnitude than those under consideration and are not directly comparable. The main object of the present experiments is to examine the structure of the different macroscopic layers of scale as a function of the metallic base and of the oxidising conditions.

#### (8) FURTHER APPLICATIONS TO COMPOUNDS OF THE SODIUM CHLORIDE AND SPINEL TYPES OF STRUCTURE.

From a broader aspect, the FeO and  $\text{Fe}_3\text{O}_4$  structures (Fig. 3) are merely examples of the sodium chloride and spinel types of structure, respectively. There are numerous systems in which these two types occur in neighbouring phases, and the structural relations described should, with appropriate modifications, also hold in those cases. Several of these phases form complete or partial series of solid solution with FeO and  $\text{Fe}_3\text{O}_4$  (*e.g.*,  $\text{MgO-MgO.Fe}_2\text{O}_3$ ), so that the difference in free energy and therefore stability of the two structures will be governed by the degree of ionic replacement. In certain of the pseudo-binary systems only the compound of the sodium chloride type, in others only that of the spinel type exists. There are definite rules controlling the stability of either structure, as a function of valencies and relative atomic sizes.

## (9) ACKNOWLEDGMENT.

The Author wishes to thank Mr. D. A. Oliver, M.Sc., F.Inst.P., Head of the Research Department, Messrs. William Jessop & Sons, Ltd., for his encouragement, and Dr. A. J. Bradley, M.A., F.R.S., and Dr. H. Lipson, F.Inst.P., of the Cavendish Laboratory, Cambridge, for constructive comments.

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### CORRESPONDENCE.

Dr. U. R. EVANS (Cambridge University) wrote: The establishment of simple crystallographic relations between  $\alpha$ -iron, wüstite and magnetite possesses an importance which can hardly be exaggerated. The author should be congratulated on his results. In applying them to the study of oxidation processes, however, it must be remembered that the changes which are crystallographically simplest are those which are most likely to lead to a stifling of the reaction, by interposition of a protective film between metal and oxygen; more complicated reactions, involving the break-up of structure, are less likely to smother themselves.

The author remarks that the facts discussed have a bearing on the problem of the corrosion resistance of steel. Presumably, high-temperature oxidation is in his mind. The rust formed in wet corrosion is essentially a precipitate. In salt water the interaction between the alkali and the iron salts formed at anodic and cathodic points, respectively, leads to hydroxides of iron, whilst in the absence of salt iron passes into water slowly as ferrous hydroxide, which throws down the less soluble ferric hydroxide or magnetite at a further distance from the metal, either by uptake of oxygen or by liberation of hydrogen. In all these cases the corrosion product, formed out of physical contact with the metal, will have no crystallographic relation to the alloy. The direct union of iron and oxygen can commence very quickly at ordinary temperatures, but soon slows itself down by isolating the iron and oxygen from one another, as shown, for instance, by the curves of Miley.<sup>1</sup> As in so many cases, it is the indirect electrochemical change, possessing little interest to the crystallographer, which produces most destruction.

Passing to high-temperature oxidation, we find that here also the changes involve factors electrochemical rather than crystallographic. According to the theory of Wagner,<sup>2</sup> which has proved fruitful in Price and Thomas' work<sup>3</sup> on the prevention of oxidation and tarnishing, the metal passes outwards through the film to meet the oxygen, not as simple atoms, but as ions and electrons. Wagner's views have this in common with those of Pfeil, quoted by the author, that it is the metal which passes outwards and not the oxygen inwards. The conception has a certain relation to the author's view that the change from ferrous oxide to magnetite consists not of an uptake of oxygen but of a loss of iron.

<sup>1</sup> H. A. Miley and U. R. Evans, *Journal of the Chemical Society*, 1937, p. 1295.

<sup>2</sup> C. Wagner and others, *Zeitschrift für physikalische Chemie*, (B) 1933, vol. 21, pp. 25, 42; 1933, vol. 22, pp. 181, 195, 199, 212, 226; 1933, vol. 23, p. 469; 1934, vol. 24, pp. 53, 59; 1934, vol. 25, p. 71; 1936, vol. 32, pp. 113, 439, 447; 1936, vol. 34, p. 309; 1937, vol. 37, pp. 148, 157; 1938, vol. 40, pp. 197, 455; *Transactions of the Faraday Society*, 1938, vol. 34, p. 851.

<sup>3</sup> L. E. Price and G. J. Thomas, *Journal of the Institute of Metals*, 1938, vol. 63, pp. 21, 29; 1939, vol. 65, p. 247.

The author attributes the absence of ferric oxide in certain cases to an energy barrier opposing the crystallographic changes. It seems more likely that it is due to the fact that he is interested in conditions where the oxygen partial pressure is below that at which ferric oxide could exist. If oxidation phenomena were usually controlled by energy barriers connected with phase changes, one would expect that the oxidation rate would be independent of the film thickness. Actually it falls off with the film thickness, and is not infrequently inversely proportional to the thickness, indicating that the controlling factor is the passage of the reactants through the film. If this is true, the passage of iron to ferric oxide, just because of the break-up of structure involved, is more likely to persist than the crystallographically simpler transformation to ferrous oxide, although the simple change may be favoured at the outset. Actually there is some evidence from my own work, admittedly not conclusive, that at relatively low temperatures ferric oxide is formed directly from the metal, and that the magnetite formed at somewhat higher temperatures, below the ferric-oxide film, is due to interaction between ferric oxide and iron. Certainly there is good evidence that in places the ferric oxide rests directly on the metal, and this will be summarised below:

A simple optical method exists<sup>1</sup> for distinguishing between a single and a double oxide film. If a strip of thin nickel is heated at one end so as to produce an oxide film of gradually diminishing thickness, a series of beautiful interference colours is produced, traceable up to the fourth order. If this specimen is cemented to celluloid (oxidised side next to the celluloid) and if from the other side the metal is dissolved away electrolytically over half the breadth of the strip, we obtain the relation between the colours of the film on the metal and those displayed by the same film when backed by air. A complementary relation is found to exist throughout the sequence, as would be expected on optical theory if the film is single. If, however, the oxide film responsible for the colours were backed by a second film which did not give colours, the reflecting basis would be the same before and after the removal of metal, and the colours would be unchanged.

Applying this test to iron, we find that the thicker films corresponding to the second- and third-order colours show precisely the same tints before and after the removal of the metal, and the reason is quite clear, since a relatively opaque layer of black magnetite is found below the ferric oxide film. But below the thin films responsible for the earlier colours of the first order the magnetite layer appears to have thinned out completely; the films are transparent, and, although the colours are weak, they show

<sup>1</sup> U. R. Evans, Fifth Report of the Corrosion Committee, *Iron and Steel Institute*, 1938, *Special Report No. 21*, p. 225.



the complementary relation. This would seem to indicate that the ferric-oxide film here rests in direct contact with the metallic iron, at least over a large part of the surface. The possibility that nests of magnetite may exist is not excluded, but they cannot extend over more than a fraction of the surface of separation between ferric oxide and iron.

I have never expressed a definite opinion as to the mechanism by which the various oxides are formed, but I incline to the view that at relatively low temperatures iron first combines with oxygen to form ferric oxide, which then under favourable conditions may interact with the metal to form magnetite along the surface of separation.

Dr. A. L. NORBURY (Birmingham) wrote: The theory, put forward in Mr. Goldschmidt's very interesting paper, of divalent ferrous ions being replaced in the lattice by trivalent ferric ions plus holes appears to have much in common with the theory put forward by the writer <sup>1</sup> to explain certain intermetallic compounds. This theory is that in certain cases atoms are replaced in the lattice by electrons or *vice versa*, so that the total number of atoms plus electrons in the lattice remains constant. It would be interesting to have Mr. Goldschmidt's views on this.

### AUTHOR'S REPLY.

The AUTHOR wrote in reply: Dr. Evans' valuable comments are much appreciated. The author fully agrees that the paper is limited to oxidation at high temperatures and is not meant to apply to wet corrosion or rusting at ordinary temperatures. Where chemical precipitation involving hydroxides is concerned, as in the case described by Dr. Evans, the crystallographic relations break down. However, the time-thickness curves of Miley and Evans were taken in dry air, and electron-diffraction work on thin films formed under similar conditions would indicate that in that case structure relations are important. Preferred orientation of one oxide phase precipitating from another, as has been reported, for instance, by Preston, Bircumshaw and Vernon,<sup>2</sup> is evidence that crystallographic as well as electrochemical factors have been prevalent.

Dr. Evans also says that in the case of high-temperature oxidation the changes involve electrochemical rather than crystallographic factors. But the author suggests that both are intimately associated, and, on the grounds of the "defect lattice" theory, may in fact be considered as two modes of expressing the same facts. Wagner's theory of the "diffusion of vacant lattice points" through the oxide

<sup>1</sup> *Journal of the Institute of Metals*, 1939, No. II., pp. 355-378.

<sup>2</sup> *Transactions of the Faraday Society*, 1935, vol. 31, p. 1668.



layer (as discussed by Mott <sup>1</sup>) agrees with this view. This "Schottky mechanism" makes essential use, for instance, of the presence of excess oxygen in  $\text{Cu}_2\text{O}$  or excess metal in  $\text{ZnO}$ , cases closely allied to that of  $\text{FeO}$ , and applied by Price and Thomas in their work on the tarnishing of copper and silver.

There is much evidence to show that crystallographic factors affect the formation of oxide films (whether protective or otherwise). Examples are as follows (chosen because they support certain suggestions made in the text):

(1) Portevin, Pretet and Jolivet <sup>2</sup> found a discontinuity in the rate of oxidation near the change point of electrolytic iron; similar breaks were observed with change of composition when the  $\gamma/\alpha$  phase boundaries were crossed on adding elements (e.g., aluminium or silicon) which close the  $\gamma$ -loop. Some recent experiments of the author also indicated such an influence of the structure of the underlying metal on the oxide; such an effect cannot be explained on a purely electrochemical basis.

(2) Fixed orientation relationships between metal and oxides have been reported by Mehl, McCandless and Rhines <sup>3</sup>; for instance, the cube plane of  $\text{Fe}_3\text{O}_4$  grows parallel to that of the parent  $\text{FeO}$ , the basal plane of hexagonal hematite parallel to the octagonal plane of magnetite. A cuprous-oxide film grown on a single crystal of copper lay with its cube axis parallel to that of the metal base (comparable with austenite and wüstite). Such orientations, which are closely related to crystal structure, are liable to influence the rate of oxidation. However, the relations between orientation and rate of oxidation will apply in the first place to thin films only. With increasing thickness the effect will be destroyed by the adaptation of atomic volumes of the crystal phases (causing, for instance, local cracking).

Regarding Dr. Evans' point that energy barriers opposing crystallographic changes are not usually the factor controlling oxidation processes, the author agrees that the diffusion of ions through the film is probably a far more potent factor. They only come into play if (external) variables, such as oxygen pressure and temperature, cause it to be in the balance whether one or the other of two crystal structures would be formed. The formation of  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$  at low temperatures is an example. Miley and Evans indicate that films formed on iron between 200° and 400° C. are  $\alpha$ - $\text{Fe}_2\text{O}_3$ , below 200° C.  $\gamma$ - $\text{Fe}_2\text{O}_3$  (cubic); under the argument of the paper the cubic oxide would still lie on the magnetite side of the "energy barrier"; in this case, a temperature of 200° C. is needed

<sup>1</sup> "Reports on Progress of Physics," 1940, vol. VI., p. 186. The Physical Society.

<sup>2</sup> *Revue de Métallurgie, Mémoires*, 1934, vol. 31, p. 219.

<sup>3</sup> Mehl, McCandless and Rhines, *Nature*, 1934, vol. 134, p. 1009. Mehl and McCandless, *ibid.*, 1936, vol. 137, p. 702.

to change the relative free energies of  $\alpha$ - and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> so as to bring about the change to the  $\alpha$  form. Generally, conditions might best be represented by free-energy curves of  $\alpha$ -Fe,  $\gamma$ -Fe, "FeO," Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, drawn as a function of oxygen content, pressure and temperature, and by determining the phases co-existing under given conditions by the method of tangents. Such a diagram might serve as a useful basis for discussion, and clarify many apparently contradictory points relating to the oxidation of iron.

By his optical method Dr. Evans demonstrated convincingly that ferric oxide can be formed in contact with the metal at relatively low temperatures. The author does not think that the paper, which is concerned with high-temperature reactions, contradicts this possibility; if the oxygen pressure is sufficiently high and reaction between iron and oxygen is allowed to proceed unimpeded, Fe<sub>2</sub>O<sub>3</sub> is liable to be produced. It would, however, be interesting to know whether the layer of ferric oxide observed in this experiment was  $\alpha$ - or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, because if it was the cubic form it would tend to support rather than conflict with the present conclusions.

The mechanism of film formation below and above 570° C. ("FeO" eutectoid point) may differ fundamentally. The author's present results on scales formed at the higher temperatures never showed Fe<sub>2</sub>O<sub>3</sub>, but always FeO in direct contact with the metal. (This is different in the case of certain alloy steels where corundum types of structure are found.) One observation may be mentioned in this connection, *viz.*, the effect of rate of cooling after oxidation. Samples of scale (comprising all layers), formed by exposing pure iron, for instance, to 650° C. for 24 hr., showed a much higher proportion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after slowly cooling than after quenching; in conformity with Dr. Evans' result, this seems to confirm the increased tendency towards the formation of ferric oxide at lower temperatures. The reason might be a microscopic cracking of the oxide film on cooling and a consequent increase of the surface of contact with oxygen. Admittedly the present results on this point are insufficient; it would be worth while to attempt to obtain direct X-ray evidence on films produced in a similar manner to those described by Dr. Evans.

The author wishes to thank Dr. Norbury for drawing attention to his paper. He agrees that an interesting parallelism exists between the intermetallic compounds that he discussed and the present oxides. The question arises to what extent the Hume-Rothery rule and other rules established for intermetallic compounds apply to the ionic bond. Dr. Norbury's idea of the "electron plus atom" lattice would permit intermetallic compounds to be considered as ionic ones with "spaceless" cations. In the oxides these sites would be occupied by the large oxygen ions; in this case the author believes that the size factor is at least as important as valencies in determining the structures. The omission of oxygen rather than of metal ions from FeO would form a more logical transition to the metallic compounds.

The sequence of structures of the electron/atom ratios 3 : 2 (body-centred cube), 83 : 52 ( $\gamma$ -brass) and 7 : 4 (hexagonal close-packed), discussed by Dr. Norbury, shows a certain analogy with FeO (NaCl type),  $\text{Fe}_3\text{O}_4$  (spinel) and  $\text{Fe}_2\text{O}_3$  (hexagonal), where the ratios would be respectively 1 : 1, 64 : 56 and 12 : 10 (*i.e.*, the total range is displaced to lower values). Dr. Norbury's "subsidiary structures" would then correspond to the defect lattices of FeO and  $\text{Fe}_3\text{O}_4$  (wüstite range and  $\gamma$ - $\text{Fe}_2\text{O}_3$ ). Both types of transition proceed by the substitution of atoms by electrons in the lattice, but this is only a formal mode of expressing the facts, which will want elaborating.

The mechanism of building up the  $\gamma$ -brass structure from 27 body-centred cubes, in which two atoms are then replaced by two electrons (*e.g.*,  $\text{Cu}^+\text{Zn}^{++} \longrightarrow \text{Cu}_{21}^+ \text{Zn}_{31}^{++}$ ) closely resembles that of deriving the spinel unit cell from 8 of the NaCl type, but an important difference is that FeO is based on the face-centred, not the body-centred, cube like CuZn.

Further, the existence of  $\gamma$ - and  $\alpha$ - $\text{Fe}_2\text{O}_3$  may be viewed in the light of Dr. Norbury's statement that the electron/atom ratios at which the body-centred cubic and close-packed hexagonal types of phases can be formed overlap considerably. In a private communication Dr. Norbury pointed out that the 12 : 10 ratio for  $\text{Fe}_2\text{O}_3$  is similar in "electron plus atom" content to the 7 : 4 ratio of the intermetallic hexagonal lattice, but a corresponding relation would not hold in the case of the other phases.

# THE DETERMINATION OF THE SOLUBILITY OF HYDROGEN IN IRON AND IRON ALLOYS.\*

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*Paper No. 4/1942 of the Alloy Steels Research Committee  
(submitted by the Hair-Line Crack Sub-Committee).*

## SUMMARY.

The solubility of hydrogen in (i) iron, (ii) a low-nickel iron alloy and (iii) a nickel steel, at various temperatures has been determined by a method which is described. It is shown that hydrogen has no effect on the critical change of iron, but in the case of the nickel-iron a sudden drop in solubility begins at a point corresponding to the peak on the thermal cooling curve and continues to a temperature of 475° C., which is 75° C. below the completion of the thermal change. This phenomenon was much more marked with the nickel steel, a fact which supports the view that carbon plays an important part in the retention of hydrogen in steel.

THE solubility of hydrogen in various metals was investigated by Sieverts in 1910,<sup>(1)</sup> and that research is generally regarded as the classical work on the subject. The value of much of the more recent work is open to question, because the investigators have used powdered metals in an attempt to reach equilibrium more quickly by increasing the surface area of the sample. In connection with work on hair-line cracks it became desirable to investigate the loss of hydrogen from solid specimens on cooling, with particular reference to the changes in solubility occurring at the  $\gamma$ - $\alpha$  transformation. Also it was desired to extend the work to steel specimens, and for this purpose a method different from that of Sieverts had to be employed.

## Apparatus.

The apparatus used in the present investigation is shown diagrammatically in Fig. 1. In principle it is similar to that employed by earlier workers; the specimen is heated in hydrogen at a known temperature and pressure until equilibrium is reached, and the amount of hydrogen dissolved by the metal is measured.

The metal specimen was contained in a Pythagoras tube, 24 in. long, of 1-in. bore and closed at one end. The open end of the tube was sealed with picein wax into a water-cooled brass block,

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the end of which was ground to make a vacuum-tight joint with a similar surface on the main part of the apparatus. By breaking

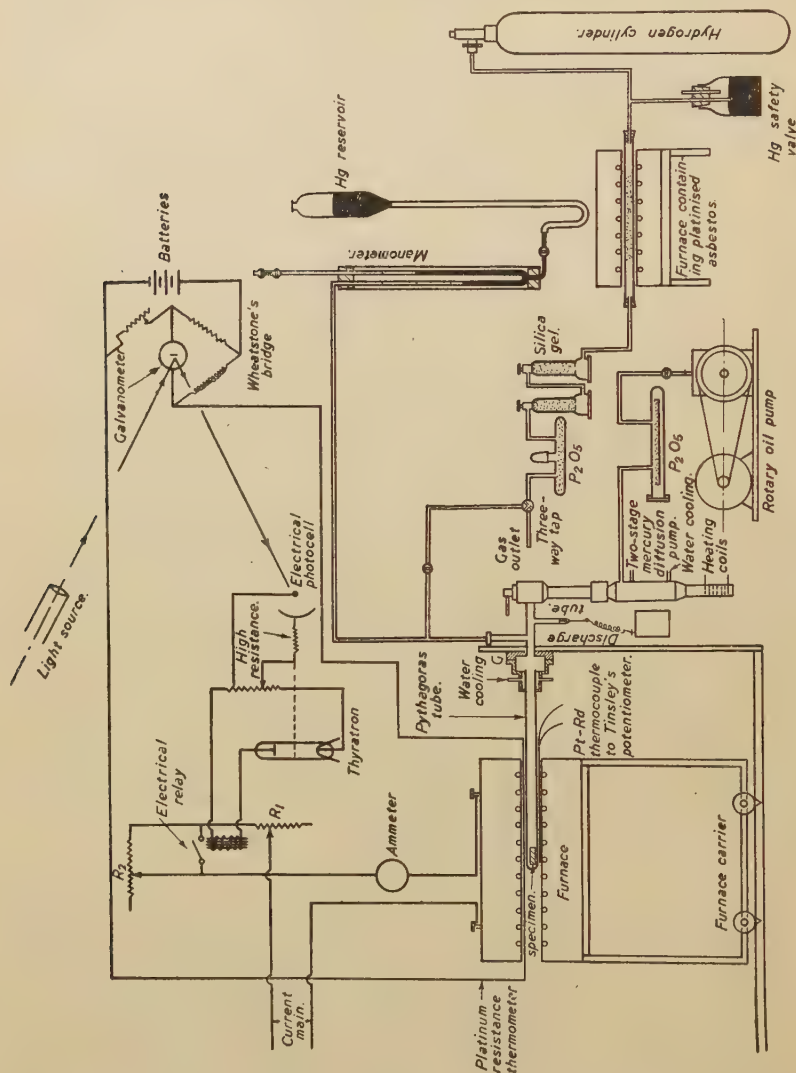


FIG. 1.—Apparatus for Hydrogen Solubility Determinations.

this ground joint, *G*, it was possible to replace the specimen without affecting the total volume of the apparatus. The tube was heated by means of a suitable wire-wound electric furnace, and



the pressure in the system was measured with a manometer of the type used in gas-analysis apparatus. This had the advantage that by changing the level of the mercury reservoir all pressure determinations could be carried out for the same fixed volume. Hydrogen could be admitted through a side tube and tap, and, when necessary, the whole apparatus, including both limbs of the manometer, could be thoroughly evacuated by a two-stage mercury diffusion pump backed by a rotary oil pump. When actual solubility determinations were in progress, the pumping system was completely isolated by means of a large-bore steel high-vacuum tap. In order to minimise the possibility of leaks, glass seals were used wherever possible and picein wax was used for metal-to-glass joints.

The hydrogen used for these experiments was passed through a long tube closely packed with platinised asbestos and heated to  $650^{\circ}$  C. To remove any water vapour thus formed, the gas was then passed through drying towers containing silica gel and finally phosphorus pentoxide before being introduced into the system.

To avoid deterioration of the platinum/platinum-rhodium thermocouple, this was attached to the outside of the Pythagoras tube, and the thermal e.m.f. was measured with a Tinsley potentiometer. Although the thermocouple was not in direct contact with the specimen, the temperature readings obtained should be accurate in view of the constant temperature conditions realised in the work. This was confirmed by the position of the iron transformation point.

Temperature control was achieved with the aid of a platinum resistance thermometer and a photo-cell and Thyatron relay. The resistance thermometer consisted of a length of 40-S.W.G. platinum wire enclosed in fine-bore silica tubing and passing from one end of the furnace to the other in close contact with the furnace walls. The thermometer formed one limb of a Wheatstone-bridge circuit with ratio arms of 10 : 1. The furnace controller could be made to operate at any desired temperature by adjusting the resistance in the fourth arm of the bridge. When the bridge was slightly out of balance because the furnace temperature was too low, the light reflected from the galvanometer mirror fell on the cathode of a gas-filled photo-electric cell of the silver/cæsium/cæsium-oxide type and caused the Thyatron relay to operate. The latter controlled an ordinary electrical relay which short-circuited part of the resistance in series with the furnace and so increased the current flowing through it. When the furnace temperature had returned to normal, the light no longer fell on the photo-cell, and the resistance  $R_2$  was once more placed in series with the furnace winding. By suitable adjustment of the resistances  $R_1$  and  $R_2$  it was possible to ensure that the temperature remained constant in spite of the fairly large fluctuations which occurred in the mains voltage. The advantages generally associated with photo-electric control were

obtained in this case, for, owing to the fact that the furnace temperature was checked continuously instead of intermittently, the temperature could be maintained constant over long periods to well within  $1^{\circ}\text{C}$ ., even at the highest temperatures employed.

### *Experimental Technique.*

The specimens first investigated consisted of a vacuum-melted iron and a nickel-iron alloy of the following compositions :

	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.
Vacuum-melted iron .	Nil	<0.02	<0.03	<0.03	<0.004	...
Nickel-iron alloy .	0.06	0.51	0.166	...	...	5.34

In order to increase the surface area and reduce the distance through which the hydrogen had to diffuse, the samples were machined into 100-g. weights of the shape of cylinders 0.75 in. in dia. and 2 in. long, with a 0.25-in. dia. hole along their axes. Before use in the solubility apparatus, the specimens were heated in a current of hydrogen at  $1000\text{--}1050^{\circ}\text{C}$ . for at least 30 days, in order to remove all traces of carbon and oxygen.

Before pressure changes due to solution of hydrogen in the sample could be determined, it was necessary to find out the pressure/temperature relationship for the apparatus without a specimen in it. Accordingly, experiments were first carried out using as blank a silica tube of shape and size identical with the metal specimens. The apparatus was thoroughly evacuated and the Pythagoras tube heated to  $1100^{\circ}\text{C}$ . for 12 hr. in order to remove any absorbed gas, and the system was then rinsed out with purified hydrogen at a few centimetres' pressure. After re-evacuation, the apparatus was filled with purified hydrogen at room temperature and a pressure of 30 cm. of mercury. The tube was then heated to  $1100^{\circ}\text{C}$ . and maintained at that temperature until equilibrium was reached. The same procedure was repeated at intervals of  $100^{\circ}\text{C}$ . down to room temperature, and from the resulting measurements the curve representing the pressure/temperature relationship for the apparatus was drawn. The results so obtained were checked to ensure that no spurious effects were observed.

Before solubility determinations were carried out on metal specimens they were heated for 12 hr. *in vacuo* at  $1100^{\circ}\text{C}$ . to remove any hydrogen remaining after the decarburising treatment. Hydrogen was then admitted to a pressure of 30 cm. of mercury at room temperature and the temperature was raised to  $1100^{\circ}\text{C}$ . and maintained there until equilibrium was reached. The equilibrium pressures were then obtained for successively lower temperatures, as in the case of the silica blank. The pressure/temperature relationships for the blank and for the two metal samples are shown in Fig. 2. Whereas with the silica blank about 3 hr. were sufficient for equilibrium to be reached, the corresponding time

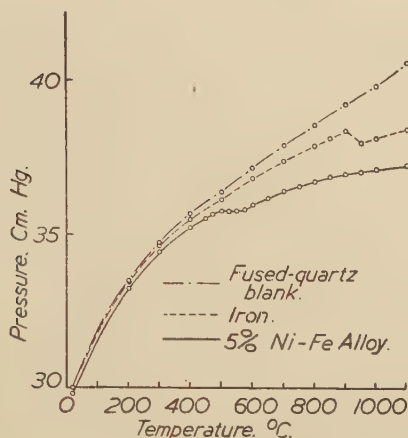


FIG. 2.—Pressure/Temperature Relationship for the Silica Blank and Two Metal Samples.

for the metal samples was much longer; thus, as shown in Fig. 3, equilibrium was attained at 1100° C. only after 7 and 4 days, respectively, as compared with about 3 hr. for the silica blank. On

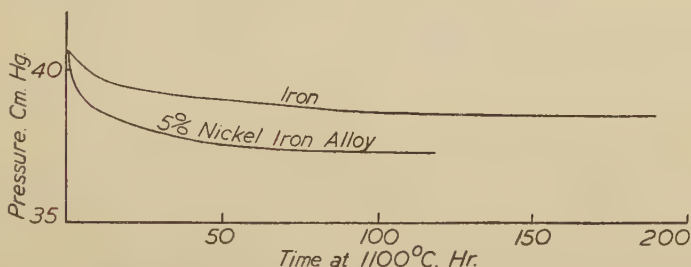


FIG. 3.—Time Required for Equilibrium to be Reached in Iron and 5% Nickel-Iron Alloys at 1100° C.

the other hand, equilibrium was subsequently reached on cooling from 1100° C. to lower temperatures in a matter of only a few hours. In all cases, however, the specimen was maintained at the same temperature for a further 24 hr. after no further pressure changes could be measured on the manometer. It was found that the time taken to attain equilibrium increased as the temperature decreased, particularly in the case of the nickel-iron alloy, and at the lowest temperatures 48 hr. were necessary.

The pressure/temperature relationship for nickel steel containing 3.8% of nickel, 0.565% of manganese and 0.22% of carbon was also determined. This was undertaken in order to study the

effect of carbon on the solubility of hydrogen in steel; the metal specimen was therefore not decarburised. For the interpretation of this result a new blank curve was necessary, and it was accordingly determined on the silica specimen along with 0.22 g. of pure graphite. The latter corresponds to the amount of carbon contained in the steel. Fig. 4 shows the pressure/temperature rela-

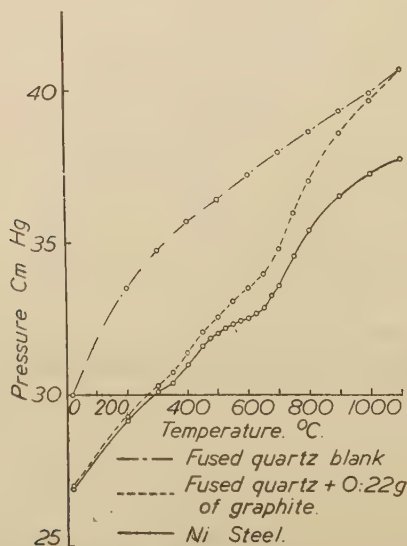


FIG. 4.—Pressure/Temperature Relationship for a 0.22% Carbon Nickel Steel and a Silica Blank containing 0.22% of Graphite.

tionships in hydrogen for the steel as well as for the blank with graphite; the old blank curve is also given, because from the difference in pressure between the old and the new one the amount of hydrocarbons formed can be calculated and will be dealt with later. It was found that the time for the steel to reach equilibrium with hydrogen was comparable to that for the nickel-iron alloy, but, whereas the time taken to reach equilibrium increased as usual at lower temperatures, the rate of evolution of hydrogen from the steel was particularly sluggish at the transformation range, in which 60 hr. were required at each successive temperature. In the case of the new blank, although at temperatures from 900° C. downwards the equilibrium between hydrogen and carbon was found to be as difficult to reach as with the steel specimen, the time required for such an equilibrium did not increase much with the decreasing temperatures, and at each temperature 48 hr. were sufficient.

*Determination of the Volume of the Apparatus.*

Before the solubility can be given in quantitative figures, the total volume of the apparatus must be known. The determination of the volume was carried out somewhat on the basis of gas analysis, for, by taking advantage of the irreversible chemical reaction between oxygen and aluminium, the measurement could be undertaken without dismantling the apparatus. The necessary experimental procedure differs from that of the solubility determination only in details. A small sample of pure aluminium contained in a porcelain combustion boat was used in place of the iron specimen, and oxygen instead of hydrogen. The metal sample was of the purest quality obtainable and contained 99.9986% of aluminium. The porcelain combustion boat had a volume approximately equal to that of the solubility specimen, and it had been repeatedly fired at 900° C. until a constant weight was obtained. After this the boat containing the sample of aluminium was carefully weighed to 0.0001 g.

The oxygen used for the experiment was passed through the furnace tube packed with platinised asbestos and heated at 650° C. After coming out of the tube the gas was led to bottles containing caustic potash and concentrated sulphuric acid; finally it was passed through drying towers containing silica gel and phosphorus pentoxide before being introduced into the furnace.

To avoid errors due to the adsorption of hydrogen by the furnace tube after solubility experiments, the system was thoroughly evacuated and then filled with purified oxygen without any specimen inside. The furnace was heated to 800° C. and the temperature maintained until no change in pressure was observed on the manometer.

After the porcelain combustion boat containing the aluminium sample was put into the furnace, the system was thoroughly evacuated and purified oxygen was admitted through the side tap to a pressure of 30 cm. of mercury and at room temperature. The pressure reading on the manometer was carefully checked and the furnace was then heated to 500° C. and maintained at that temperature until a sufficient quantity of oxygen had been consumed. The pressure reading was again taken after the furnace had cooled to room temperature, and the combustion boat containing the sample was taken out and weighed. From the difference in weight of the aluminium sample before and after oxidation, the amount of oxygen combined as oxide could be calculated. The total volume of the system is then given as :

$$V = \frac{76}{P_1 - P_2} \times (\text{volume at N.T.P. of oxygen consumed}),$$

where  $P_1$  = the pressure reading at room temperature before oxidation,  
 $P_2$  = the pressure reading at room temperature after oxidation.

By this method the total volume of the apparatus was found to be 360 c.c.



*Results.*

It can be shown that under the conditions of the solubility experiments, the volume of gas absorbed by the specimen is :

$$0.395V \left( \frac{P_q - P_s}{P_q} \right) \text{ c.c. (at N.T.P.),}$$

and the solubility is :

$$0.395V \left( \frac{P_q - P_s}{P_q} \right) \cdot \frac{100}{W} \text{ c.c. per 100 g. of metal (N.T.P.),}$$

where  $V$  = the total volume of the system in cubic centimetres,  
 $P_s$  = the equilibrium pressure of hydrogen for metal at temperature  $T$ ,  
 $P_q$  = the equilibrium pressure of hydrogen for the blank at the same temperature  $T$ ,  
 $W$  = the weight of the metal specimen in grammes.

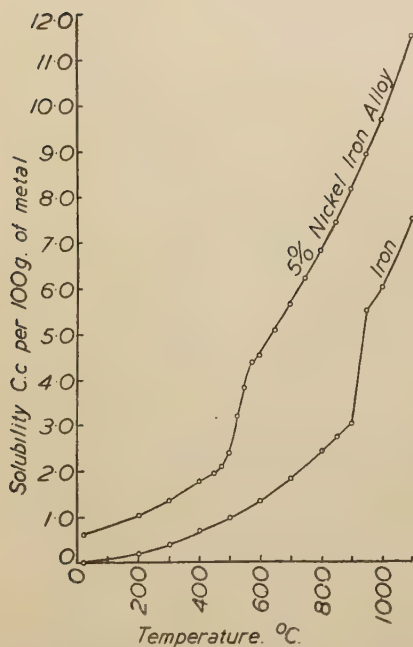


FIG. 5.—Hydrogen Solubility in Vacuum-Melted Iron and a 5% Nickel-Iron Alloy at Various Temperatures.

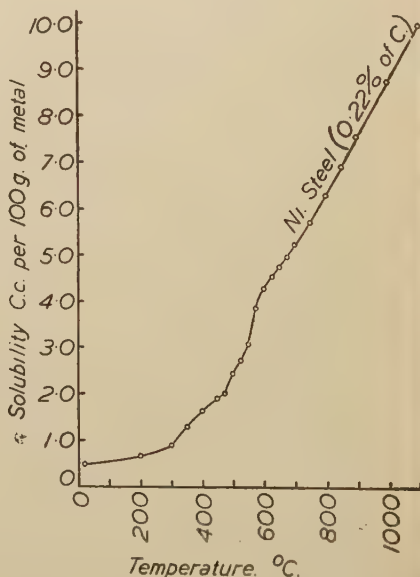


FIG. 6.—Hydrogen Solubility in a 0.22% Carbon Nickel Steel at Various Temperatures.

The values of the solubility for the vacuum-melted iron and the nickel-iron alloy are given in Fig. 5 and of that for the nickel steel in Fig. 6.

It will be seen that an abrupt change in solubility occurs between  $950^{\circ}$  and  $900^{\circ}$  C. on cooling the iron specimen and that the temperature coefficient of solubility is greater in  $\gamma$ -iron than in  $\alpha$ -iron. In Table I. the results are compared with those for electrolytic iron and reduced iron redetermined by Sieverts<sup>(2)</sup> and other independent workers<sup>(3)</sup> recently.

TABLE I.—*Solubility of Hydrogen in Iron according to Various Authorities.*

Research Workers.	Hydrogen, C.c. per 100 g. Iron at N.T.P. at—			
	500° C.	700° C.	900° C.	1100° C.
Present investigation . . . . .	1.0	1.8	3.1	7.5
Sieverts, Zapf, Moritz, 1938 <sup>(2)</sup> . .	0.6	1.8	3.0	7.0
Iwase and Fukusima, 1938 <sup>(3)</sup> . . .				
Electrolytic iron . . . . .	0.5	1.6	2.8	7.2
Reduced iron . . . . .	0.7	1.9	3.2	6.8

Although the agreement between the values given in Table I. is good, it must be remembered that in the present work the solubilities were determined at pressures between 30 and 41 cm. of mercury, as compared with the normal pressure of 76 cm. employed by other workers. Thus, without assuming the quantitative validity of Sieverts' law, it appears that the solubilities given here would be higher for corresponding pressures than those determined by Sieverts, and it may be of interest to consider the two methods. In the classical method due to Sieverts, the solubility is determined at successively *higher* temperatures, and at each temperature, as soon as it is detected that some gas has gone into solution, more hydrogen is admitted to restore the pressure to 76 cm. of mercury. Strictly speaking, true equilibrium can never be reached in this manner, and, owing to the method by which equilibrium is approached, the solubility values would tend to be too low. As the present authors desired to correlate solubility values with loss of hydrogen from steel on cooling, the method that they adopted consisted in saturating the metal at  $1100^{\circ}$  C. and subsequently allowing equilibrium at successively *lower* temperatures to be reached by evolution of gas from the specimen. This method had the advantage that equilibrium was reached more quickly than on a rising temperature, but the solubility values obtained would, if anything, tend to be too high, owing to the retention of hydrogen by the metal. It is probable that the true solubility values lie between those obtained by the two methods.

In the case of the nickel-iron alloy, the discontinuity was observed at  $575$ – $475^{\circ}$  C. The transformation was so sluggish that it was possible to obtain readings in the middle of this temperature range. The nickel steel gave a similar type of curve (Fig. 6), the

discontinuity of the solubility in this case being even more drawn out, and covering a temperature range from 600° right down to 300° C.

It has been shown in Fig. 4 that the difference in pressure between the first and second blank curves must be due to the formation of hydrocarbons in the latter case. Assuming that the hydrocarbons formed consist entirely of methane, and since the formation of methane from hydrogen involves a change from two volumes to one volume, the decrease in volume itself is equal to

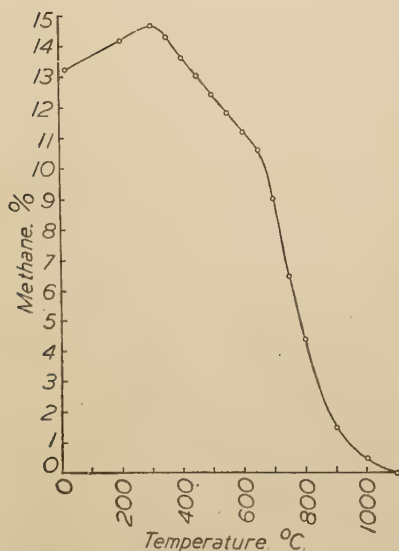


FIG. 7.—Percentages of Methane Found, calculated on the assumption that the hydrocarbons formed consist entirely of methane.

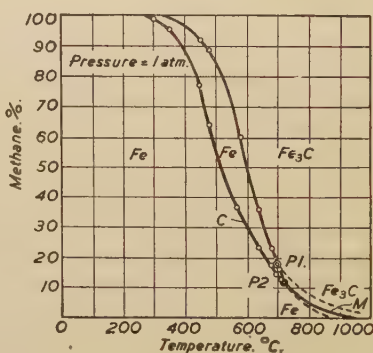


FIG. 8.—Schenck's Results with Methane.<sup>(4)</sup>

the volume of methane formed. It is then obvious that the volume of methane formed can be expressed as :

$$V_{\text{CH}_4} = 0.395 V \left( \frac{P_q - P_c}{P_q} \right) \text{ c.c. (at N.T.P.),}$$

where  $P_q$  = the equilibrium pressure in the system for the silica blank at temperature  $T$ ,

$P_c$  = the equilibrium pressure in the system for the blank with carbon at the same temperature  $T$ ,

$V$  = the total volume of the system.

Knowing the total amount of hydrogen admitted into the system, the amount of methane formed can be easily expressed in percentages. The results are plotted in Fig. 7.

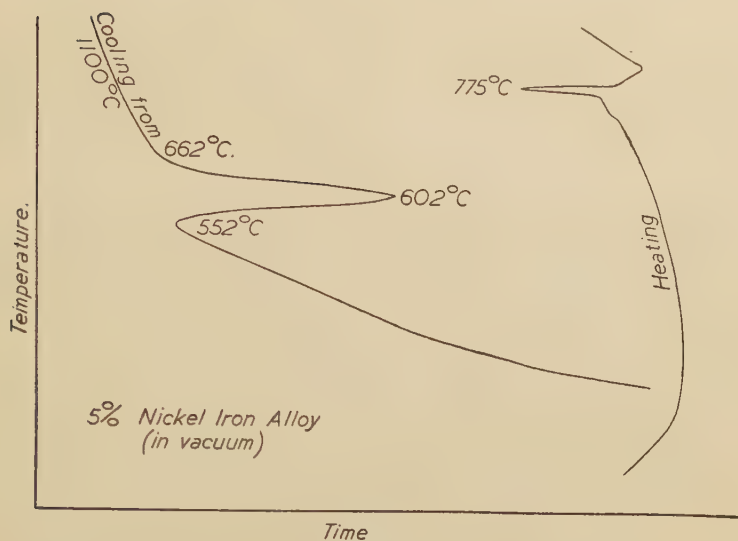


FIG. 9.—Thermal Curves for the Nickel-Iron Alloy after the Solubility Determination.

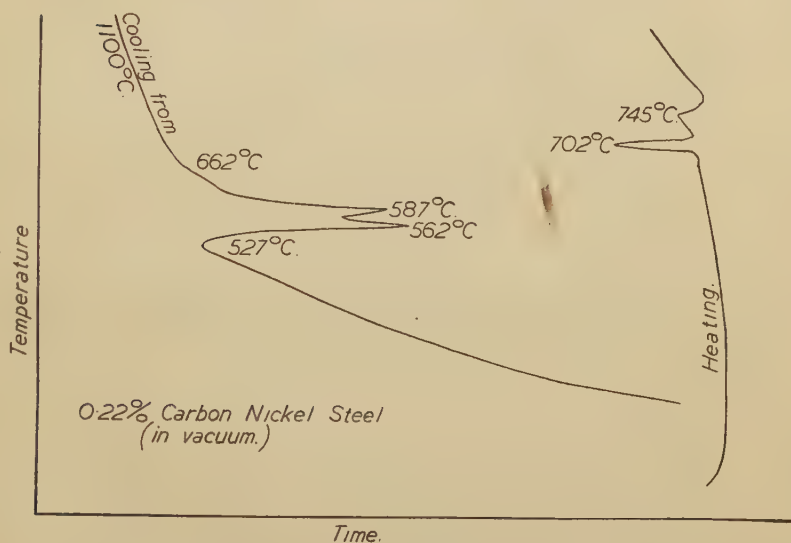


FIG. 10.—Thermal Curves for the Nickel Steel after the Solubility Determination.

It is interesting to note that the curve showed a maximum at 300° C.; after that the amount of methane decreased with an increase of temperature. The rate of decomposition became more rapid beyond 650° C., and at 1000° C. or above there was practically no methane present. Similar equilibrium relationships of the reactions :



were worked out by Schenck,<sup>(4)</sup> who used a gas consisting of nearly pure methane at a pressure of 1 atm. His experiments covered the temperature range between 300° and 1000° C., and the results are reproduced in Fig. 8. A comparison of Figs. 7 and 8 will reveal that these two curves for the corresponding temperature range are not unlike, bearing in mind the fact that they were carried out under widely different concentrations and pressures.

Figs. 9 and 10 are thermal curves for the nickel-iron alloy and the nickel steel respectively, both being heated *in vacuo* after the solubility determination. They are presented for the interest of comparison with the transformation temperatures given by the solubility curves.

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[This paper was discussed jointly with the two following papers on "The Formation of Hair-Line Cracks," Part I. by Professor J. H. Andrew, A. K. Bose, G. A. Geach and H. Lee, and Part II. by Professor J. H. Andrew, A. K. Bose, H. Lee and A. G. Quarrell.]



# THE FORMATION OF HAIR-LINE CRACKS. —PART I.\*

BY PROFESSOR J. H. ANDREW, D.Sc., A. K. BOSE, B.Met., G. A. GEACH, M.Sc., Ph.D., AND H. LEE, B.Eng., Ph.D. (THE UNIVERSITY OF SHEFFIELD).

*Paper No. 5/1942 of the Alloy Steels Research Committee (submitted by the Hair-Line Crack Sub-Committee).*

(Figs. 2 to 16 = Plates VI. to VIII.)

## SUMMARY.

The work of Musatti and Reggiori has been confirmed, showing that the soaking of alloy steels in hydrogen at 1200° C. followed by rapid cooling through the  $A_1$  point results in the formation of internal defects similar to hair-line cracks. The cracks were not found in specimens examined immediately after quenching, but only after an ageing period. Such defects were not observed when the soaking at 1200° C. was carried out *in vacuo* or in nitrogen, followed by water-quenching. The conclusions are therefore drawn that the cracks cannot be due solely to the stresses resulting from the drastic heat treatment and that hydrogen must be regarded as the major factor operative in hair-line crack formation.

Evidence was obtained that when cracks had been formed they contained hydrogen. Thus, as a result of rapid heating to 300° C., white ferrite veins surrounded the cracks, whilst after similar rapid heating to 650° C. globular carbides were observed instead. The suggestion is made that the white ferrite veins are due to decarburisation by the hydrogen contained in the cracks immediately after formation. Decarburisation results in the formation of methane, which is increasingly unstable above 600° C. in contact with steel. Accordingly, rapid heating to 650° C. results in the precipitation of carbide on the surfaces of the crack. It is therefore to be concluded that carbide segregation along the cracks is a result and not the cause of cracks.

In addition to the white veins of ferrite surrounding the cracks in tempered specimens, quite distinct white filaments of an austenitic character were observed in hydrogen-treated and quenched specimens. The gradual disappearance of these white filaments at room temperature is in keeping with the view that they consist of a hydrogen-rich constituent which owes its stability, at any rate in part, to its hydrogen content.

THE experimental work to be described in Part I. was undertaken at the suggestion of the Hair-Line Crack Sub-Committee with the object of proving or disproving the work of Musatti and Reggiori.<sup>(1)</sup> The most important feature of their work is that internal defects

\* Received 30th June, 1942. This paper is published by authority of the Alloy Steels Research Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

similar to hair-line cracks were produced by soaking steel specimens in hydrogen at a high temperature followed by rapid cooling. This has been confirmed in the present work, but during the course of the investigation other aspects of the problem became prominent, leading to experiments of a more divergent nature. For the most part the results of these experiments will be reported at a later date.

### EXPERIMENTAL.

The three steels used for most of the present work are described in Table I. Steels *F4* and *F5* were crucible melts made in the

TABLE I.—*Steels Investigated.*

Steel.	Composition.					Ac. ° C.	Ar. <sup>*</sup> ° C.
	C. %.	Mn. %.	Ni. %.	Cr. %.	Mo. %.		
<i>F1</i>	0.28	0.26	3.13	1.35	0.31	710	420
<i>F4</i>	0.61	0.80	...	...	...	748	680
<i>F5</i>	0.22	0.57	3.8	...	...	700	570

\* On cooling from 900° to 350° C. in 2½ hr.

Metallurgical Department, Sheffield University, 50-lb. charges being cast into moulds 3 in. square. Steel *F1* was made in a high-frequency furnace and was obtained in the form of billets 4 in. and 5 in. square from a 3-cwt. cast. These were all forged to 1¼-in. round bars. The specimens used were cylinders 4 cm. long and 4 cm. in dia. cut from these bars.

Preliminary experiments on specimens of this size showed that cracks could be repeatedly produced by soaking for 18 hr. in hydrogen at 1200° C. followed by water-quenching and ageing at room temperature. For comparison, the treatment described by Musatti and Reggiori for cylinders 8 cm. long and 6 cm. in dia. consisted of soaking for 7 hr. at 1150° C. followed by water-quenching.

The specimens were heated in hydrogen in a Pythagoras tube closed at one end, the open end being fitted with a water-cooled bung which carried a long gas inlet tube and a short gas outlet tube. Three specimens were placed near the closed end of the tube, which was heated in a wire-wound tube furnace. Hydrogen was passed into the tube during the heating to 1200° C. which took about 3 hr., and for the soaking period of 18 hr. at that temperature. The hydrogen was then swept from the tube by passing nitrogen for 6 min., after which the bung was removed and the specimens were at once tipped into cold water, which was stirred during the quenching. Before entering the tube, the gases were passed through alkaline pyrogallol solution and through towers containing calcium chloride and activated alumina.

Before examination, the quenched specimens were aged at room

temperature for at least 24 hr. Since the steel *F4* could not be cut in the as-quenched condition, tempering was necessary. In order to maintain similar conditions for all three steels, the same tempering treatment was given in all cases except where otherwise stated below. A transverse slice was cut from the centre of each specimen and one half was macro-etched in boiling hydrochloric acid to reveal hair-line cracks, whilst microsections were prepared from the other half. A second slice was quenched from 800° C. and fractured along a diameter to expose flakes. Any variations made in this procedure during the investigation are mentioned in the following record of the results obtained.

## RESULTS.

*General.*—When the usual cylindrical specimens of steels *F1*, *F4* and *F5* were given the standard hydrogen treatment described above, numerous cracks were observed in the transverse section, Fig. 2, whilst the fracture showed discontinuities resembling flakes in corresponding positions. The cracks appeared in an annular zone 3–5 mm. below the surface of the cylinder, surrounding a sound core into which occasional long cracks penetrated. If the specimen was sectioned immediately after quenching, no cracks were observed, as shown in Fig. 2. It was found that in all cases specimens of *F1* and *F5* showed more numerous cracks than specimens of *F4* which had received the same treatment.

*The Effect of Variations in the Specimens.*—With a view to determining whether the radial distribution of the cracks had any connection with residual forging or rolling stresses in the steel, two cylinders 10 cm. long by 4 cm. in dia. were machined from the 4-in. square billet of steel *F1*, one with its axis parallel to that of the billet and the other perpendicular to it. Both specimens were given the standard hydrogen treatment, and after ageing both gave the normal crack distribution.

The effect of the shape of the specimen upon the crack distribution was also studied. A conical specimen, tapering from 4 cm. to 0.8 cm. in dia. and with cylindrical ends to eliminate possible end effects, was machined from the steel *F1*. This was soaked in hydrogen and treated in the usual manner, after which it was cut into transverse slices on which the distribution of cracks in the cone was measured. The corresponding crack distribution is reproduced diagrammatically in Fig. 1, from which it will be observed that the crack zone tended to conform to the shape of the specimen, and that no cracks were observed in those parts of the specimen which were less than 2 cm. in dia. This experiment was repeated with steel *F5* and similar results were obtained.

An unforged specimen of each steel was cut from the ingot and each was given the standard hydrogen treatment simultaneously with the normal specimen from the forged bar. Cracks formed in

the forged steels, but were not observed in the as-cast specimens. As shown in Fig. 3, the structure of the as-cast specimens was very coarse. Cracks were always obtained in forged specimens of steels *F1* and *F5* which had been given the hydrogen treatment, but were far fewer in similar specimens of *F4* which had undergone the same reduction on forging. On the other hand, when a short length of the steel *F4* was reformed, being twice up-ended and forged back to its original form, cracks were obtained in abundance after the standard hydrogen treatment.

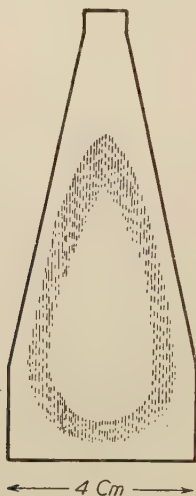


FIG. 1.—The Distribution of Cracks within a Conical Specimen. All the cracks occurred in the shaded area.

In order to investigate further the effect of forging upon crack formation, 50 lb. of steel *F1* were remelted and cast into an ingot 3 in. square. From this a cone, tapering from 6.5 cm. to 4.5 cm. in dia., was turned and forged to a bar 4.5 cm. in dia. Specimens were cut from the bar at various positions corresponding to suitable forging reductions, machined to 4 cm. in dia. and given the standard hydrogen treatment. Cracks were observed in all specimens where the reduction in forging was more than about 30%, and the number of cracks appeared to increase slightly with the degree of forging.

*The Effect of Modified Treatments.*—Specimens heated in nitrogen to 1200° C. and then soaked in hydrogen for 4 hr. prior to water-quenching developed cracks as usual. In a single experiment carried out with steel *F1*, many cracks were observed after soaking for only 2 hr. in hydrogen, the specimen being water-quenched from 1200° C. as usual. There seems to be no doubt, therefore, that the soaking time normally used was adequate to produce cracks in the steels employed.



Experiments were made to determine the effect of different cooling conditions upon crack formation. A piece of steel *F1* was allowed to cool from 1200° C. on an asbestos sheet in still air, but no cracks were observed after ageing and tempering. Three similar pieces were soaked in hydrogen and then air-cooled to a definite temperature, measured by thermocouples inserted in small axial holes, before they were water-quenched. It was found that the specimens which were quenched from 800° C. and 600° C. respectively showed cracks, but the third specimen, which was quenched from 400° C., was free from cracks ( $Ar_1 = 420^\circ \text{C.}$ ).

From a similar result, Matsuyama, Sasakawa and Iki <sup>(2)</sup> advanced the theory that the specimens must be quenched through the  $Ar_1$  point if cracks were to be formed. To decide whether it is actually the  $Ar_1$  point or merely a sufficiently high temperature regardless of the  $Ar_1$  point that is required, the experiment was carried out with the steel *F4*, which has a higher change point. In addition, the  $Ar_1$  point at 680° C. was more closely "bracketed." The results obtained confirm the hypothesis. Thus, numerous cracks were observed in the specimens which were quenched from 1200° or 705° C. respectively, but the specimen quenched from 650° C., that is, just below the main change point, showed no cracks at all.

With a view to investigating the effect of quenching to a temperature other than room temperature, three specimens of *F1* were given the standard soaking in hydrogen at 1200° C. and then quenched in oil at 150° C. The specimens were then given the following treatments: (a) Held at 150° C. for 1 hr., cooled to room temperature and aged for 45 hr., softened and sectioned, (b) aged for 45 hr. at 150° C., cooled to room temperature and immediately softened, and (c) aged for 45 hr. at 150° C. and annealed at 600° C. without first cooling. Cracks were not found in any of the specimens.

*The Ageing Period.*—In preliminary experiments two pieces of steel *F1* were hydrogen-treated and quenched together; one was cut immediately after quenching and the other aged several days before sectioning. Complete transverse sections from these specimens are shown in Fig. 2, from which it will be seen that cracks developed only after ageing.

In order to determine whether cracks were formed gradually or developed suddenly, several specimens of steel *F1* were hydrogen-treated and aged for different periods before being examined. It was found that specimens sectioned on the day of quenching invariably showed no cracks, whereas when similar specimens were aged overnight, cracks were obtained. Further ageing did not materially increase the number of cracks, which would appear to indicate that the cracks were formed rapidly within a short period of time.

It was not found possible to locate the incubation period more closely, because the results obtained by sectioning different speci-



mens tended to be somewhat inconsistent. Other experiments are being carried out, however, and will be reported later.

*Control Experiments.*—Since prolonged soaking at  $1200^{\circ}\text{C}$ . followed by water-quenching is a drastic heat treatment which might itself cause cracks as a result of the stresses set up, control experiments were carried out in which nitrogen replaced hydrogen. Specimens were soaked in nitrogen at  $1200^{\circ}\text{C}$ . and then quenched, aged and examined as usual. Specimens which had been treated in this manner did not show cracks.

*Microscopic Examination.*—Such microscopic work on hair-line cracks as can be found in the literature is exceedingly fragmentary, and therefore a detailed micro-examination was made during the course of the present investigation.

The published work can be briefly summarised as follows : Maurer and Korschan <sup>(3)</sup> stated that true flakes were transcrystalline and they drew a distinction between them and intergranular fissures. Some workers <sup>(4)</sup> have thought that a connection existed between hair-line cracks and inclusions, whilst others <sup>(5)</sup> have found no such relation. Aichholzer <sup>(6)</sup> suggested that carbide segregation caused the formation of cracks. Klausting <sup>(7)</sup> found flake formation to be linked with the presence of martensite in his steels, and observed that the treatments which prevented crack formation were also those which prevented the formation of martensite.

The first series of microsections examined were cut from the specimens which had been hydrogen-treated, water-quenched, aged and then tempered by rapid heating to  $300^{\circ}\text{C}$ . For the most part the cracks were intercrystalline, but, as shown in Fig. 4, the same crack may be partly intercrystalline and partly transcrystalline. After etching in Vilella's reagent, which, it is claimed, distinguishes the original austenite grains, the cracks were very largely, but not wholly, transcrystalline (Fig. 5). These results do not support Maurer and Korschan's suggestion that the two types of cracks are distinct.

When the specimens were rapidly heated to  $300^{\circ}\text{C}$ . before sectioning it was found that white veins of ferrite formed along the cracks, as shown in Fig. 6, the matrix being a finely divided mixture of sorbite and ferrite. These veins were not found around every crack examined, particularly in steel *F4*, but were usually present. They were not found in steel *F5* which was tempered at  $220^{\circ}\text{C}$ ., but appeared in a similar specimen tempered at  $310^{\circ}\text{C}$ . Furthermore, no such veins occurred in specimens of any of the steels examined if the heating to tempering temperature was slow. Indeed, in order to be sure of obtaining these white veins of ferrite around the cracks, the specimen was placed in a furnace which was already at  $700^{\circ}\text{C}$ . The furnace was switched off immediately the specimen was introduced, and experiments showed that the heat capacities of the furnace and the specimen were such that the maximum temperature reached by the specimen was  $300^{\circ}\text{C}$ . This temperature was reached much

more quickly under these conditions than if the specimen had been heated simultaneously with the furnace, or placed in a furnace which was already at 300° C.

Confirmation that these white veins were indeed ferrite can be obtained from Fig. 4, which was taken at such a high magnification that ferrite is clearly shown along the cracks. In addition, when microstructures of steel *F5*, which showed the white veins, were heated for 2 hr. *in vacuo* at different temperatures and then slowly cooled, no change was observed if the temperature was below 700° C.; similar treatment at 750° C., however, resulted in a disappearance of the white veins.

When specimens showing cracks were tempered at 650° C. instead of 300° C., macro-etching with Oberhoffer's reagent revealed that the cracks were in the impure areas (Fig. 7), but no consistent relationship was found between the orientation of the cracks and the primary dendrites. Some of the cracks appeared to be parallel to the dendrites (Fig. 8), whilst others were inclined, even in the same section (Fig. 7).

Apparent segregation of carbide was evident near the cracks in the specimens which had been tempered at 650° C. In these sorbitic structures, carbide globules accumulated along the cracks (Fig. 9), and as chains extended beyond them (Fig. 10). Etching in alkaline sodium picrate darkened these segregated particles (Fig. 11), showing that they were carbide. This carbide segregation was not obtained in specimens which had been quenched, aged and tempered after soaking *in vacuo* or in nitrogen.

At about the same time as the inception of the authors' work, Oliver and Pinder<sup>(8)</sup> found white veins in a particular sample of air-hardening nickel-chromium-molybdenum steel which had been forged and subsequently softened at 650° C. From an independent microscopical and X-ray examination they concluded that the principal constituent of the veins was ferrite, which had been formed by the decarburisation of the steel by hydrogen. The presence of occasional carbides in the white veins was also noted, but no explanation of their occurrence was given. These results, obtained by independent workers upon industrial samples, confirm the authors' own findings from more extended laboratory investigations.

In the present work, microstructures were also examined immediately after quenching and without tempering. Sections were cut from at least  $\frac{1}{4}$  in. below the surface of the specimens, and care was taken to keep these cold during their preparation. Steel *F4*, as quenched, was too hard to saw, but steels *F1* and *F5* could be cut and examined. The preparation of the microsections took about 2 hr. The structures obtained are shown in Figs. 12, 13 and 14. The specimens revealed no cracks, and in general the microstructure was what would be expected in steel of this composition and heat treatment. In one respect, however, the structure was abnormal,

in that a white constituent in the form of filaments at the grain boundaries was observed. These filaments were best seen at a magnification of 800, when they appeared as a frequent and prominent feature of the microstructure. In similar specimens soaked in nitrogen instead of hydrogen, however, such filaments could only be found after long and careful exploration of the microsection, and even then the filaments were much less prominent than those in the hydrogen-treated specimens.

The specimen shown in Fig. 14 was aged for 14 days, repolished, etched and examined once more. It will be seen by comparing Fig. 15 with Fig. 14, that the white filaments had almost disappeared, although the background structure was only slightly affected by the repolishing. No cracks were observed in the microsection after ageing, but this was not surprising, since cracks had not yet been found to develop in a free surface. In an attempt to correlate hair-line cracks with these white filaments, specimens which had been hydrogen-treated and water-quenched were aged before sectioning. It was found that the white filaments were less numerous in specimens showing cracks than in the unaged specimens, but it was not possible to obtain any closer correlation.

It is suggested that this unstable white constituent contained hydrogen which diffused away during ageing, thus leading to the destruction of the constituent. On etching in Stead's reagent, the white constituent was unaffected even after prolonged etching (Fig. 16). Its behaviour on etching, both in alcoholic nitric acid and in cupric reagents, resembled that of austenite.

#### SUMMARY AND CONCLUSIONS.

The experimental results given above confirm the conclusion of Musatti and Reggiori that internal defects similar to hair-line cracks can be produced in solid steels by soaking in hydrogen at a high temperature followed by rapid cooling through the  $Ar_1$  point. Furthermore, the cracks are not formed immediately after quenching, but an ageing period is required. This suggests that the cracks are not due solely to the stresses resulting from the drastic heat treatment which the specimens have undergone, and further evidence in support of this view is afforded by the fact that a similar heat treatment *in vacuo*, or in nitrogen, followed by water-quenching does not cause such defects. It follows, therefore, that hydrogen must be regarded as the major factor operative in hair-line crack formation.

Certain of the results obtained are in keeping with the hydrogen pressure theory put forward by Bennek, Schenck and Müller.<sup>(9)</sup> Thus, cracks were never found to develop at a free surface, even at the surface exposed by sectioning a freshly quenched specimen. In all cases the cracks were at least 3 mm. below the surface of the specimen. Again, the fact that no cracks were obtained in cast



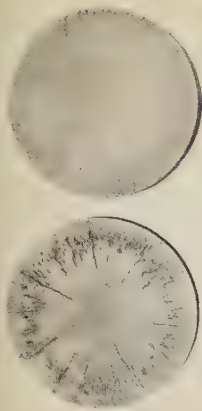


FIG. 2.—Steel F1, treated and aged 10 min. (top) and 3 days (bottom). Deeply etched in boiling hydrochloric acid.  $\times 150$ .

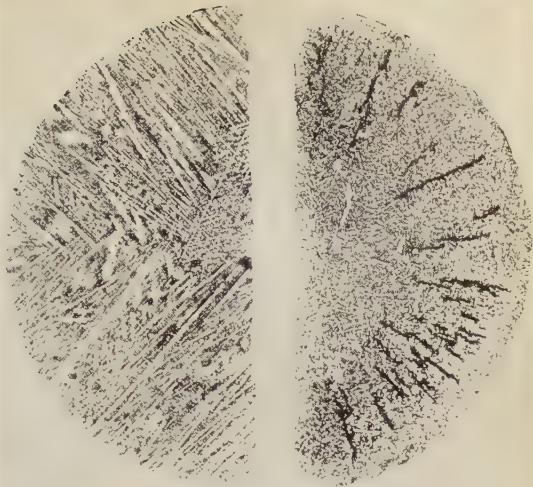


FIG. 3.—Steel F5, after treatment. Left, as cast; right, forged.  $\times 24$ .

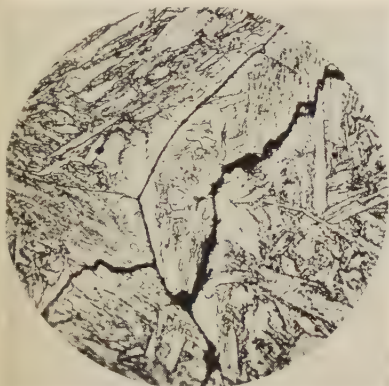


FIG. 4.—Steel F5, hydrogen-treated, quenched, aged, and tempered at  $300^{\circ}\text{C}$ . Etched in 2% nitric acid.  $\times 1300$ .

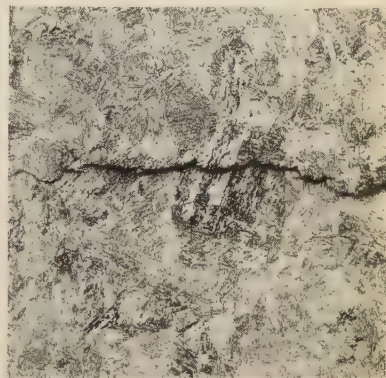


FIG. 5.—Steel F1, etched in Vilella's reagent.  $\times 75$ .

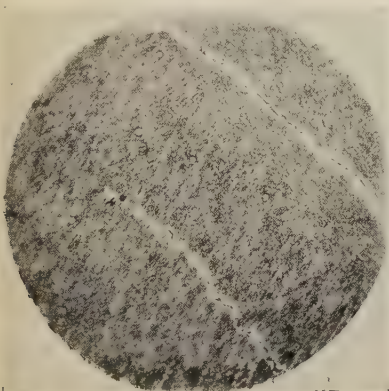


FIG. 6.—Steel F4, tempered at  $300^{\circ}\text{C}$  after hydrogen treatment, quenching and ageing. Etched in 2% nitric acid.  $\times 400$ .

(Micrographs reduced to two-thirds linear in reproduction.)



FIG. 7.—Steel F4.

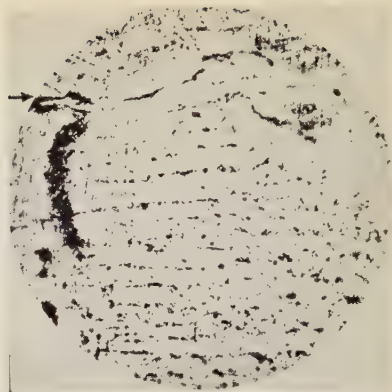


FIG. 8.—Steel F4.

FIGS. 7 and 8.—Steel F4, hydrogen-treated, quenched, aged, and tempered at 650° C. Etched in Oberhoffer's reagent.  $\times 10$ .

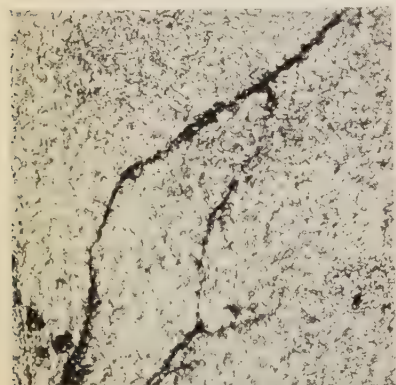


FIG. 9.—Steel F4, fully tempered at 650° C. Etched in 2% nitric acid.  $\times 1500$ .

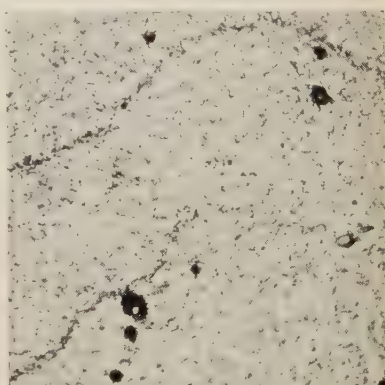


FIG. 10.—Steel F4, continuation of cracks shown in Fig. 9. Etched in 2% nitric acid.  $\times 1500$ .

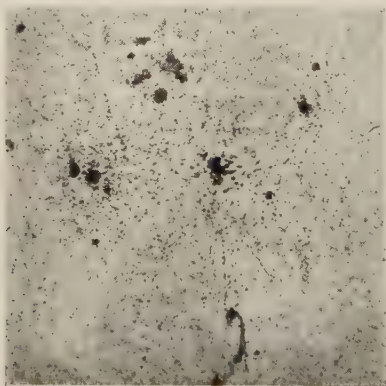


FIG. 11.—Steel F4, same as Figs. 9 and 10 but etched in boiling sodium picrate.  $\times 800$ .

(Micrographs reduced to two-thirds linear in reproduction.)



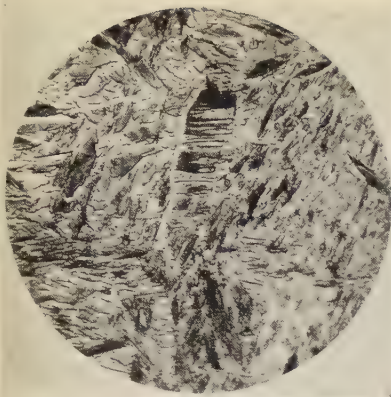


FIG. 12.—Steel F1.

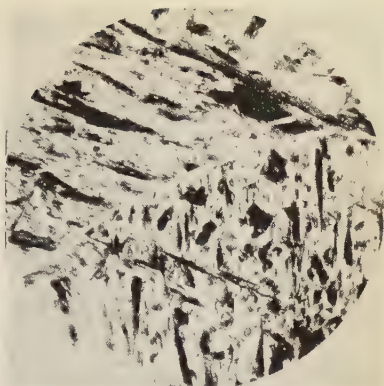


FIG. 13.—Steel F5.

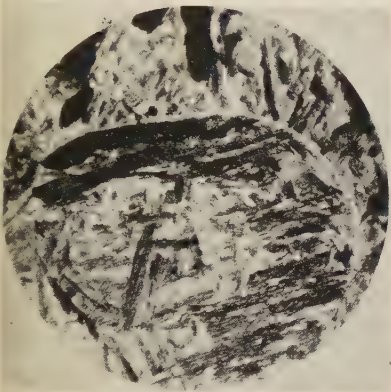


FIG. 14.—Steel F5.

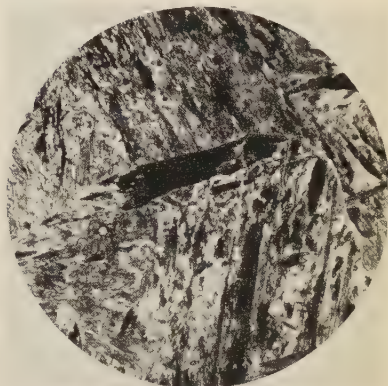


FIG. 15.—Steel F5, same as Fig. 14, aged 14 days, repolished and etched in 5% nitric acid.

FIGS. 12 TO 15.—Specimens Soaked in Hydrogen at 1200° C. and Water-Quenched. Etched in 5% nitric acid.  $\times 800$ .

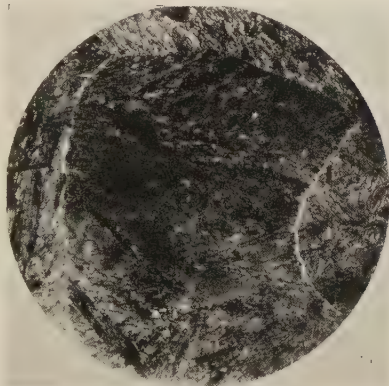


FIG. 16.—Steel F5, quenched structure after hydrogen soaking. Deeply etched in Stead's No. 1 reagent.  $\times 800$ .

(Micrographs reduced to two-thirds linear in reproduction.)



specimens under the conditions described could be attributed to the open structure of the steel in question.

Whether the hair-line cracks are due to the diffusion of hydrogen into voids or to the breakdown of a hydrogen-rich constituent it is not possible to decide at present. Evidence was obtained, however, that when the cracks had been formed they contained hydrogen. Thus the occurrence of white ferrite veins around the cracks on rapid heating to  $300^{\circ}\text{C}$ . and of globular carbide on heating to  $650^{\circ}\text{C}$ . before sectioning can be explained as follows: During the crack formation at room temperature molecular hydrogen is stored in the cracks. If heating to  $300^{\circ}\text{C}$ . is slow, this hydrogen breaks down to the atomic state, diffuses through the metal and escapes into the surrounding atmosphere. With rapid heating, however, little gas escapes by diffusion, and, instead, decarburisation of the metal surrounding the crack occurs with the simultaneous formation of methane, which is unable to diffuse through the metal. As shown in a separate paper,<sup>(10)</sup> the temperature of maximum stability of methane in contact with steel is  $300^{\circ}\text{C}$ ., whilst methane becomes very unstable above  $600^{\circ}\text{C}$ . Accordingly, when the cracks containing methane are heated to  $650^{\circ}\text{C}$ . the methane decomposes with the deposition of carbide along the cracks, whilst the hydrogen set free diffuses through the metal. Thus, the apparent carbide segregation along the cracks observed in this work as well as by Aichholzer is the *result* of crack formation and not the *cause*.

Some evidence for the existence of a hydrogen-rich constituent was obtained. Thus the gradual disappearance of the white filaments from hydrogen-treated and quenched specimens is in keeping with the suggestion, already made, that these white filaments are a hydrogen-rich constituent which owes its stability, at any rate in part, to its hydrogen content.

Although all cracks were obtained by soaking the solid metal in hydrogen, there is no reason to suppose that the mechanism of crack formation is any different from that involved in steelmaking practice. Thus, molten steel may pick up hydrogen and retain it after solidification, and although a steel ingot may contain little or no hydrogen immediately after casting, the possibility of hydrogen contamination during heat-treatment operations should not be overlooked.

It is not proposed at this stage of the work to suggest a complete theory of hair-crack formation, but all the results so far obtained are in keeping with the view that hydrogen is the most important single factor involved.

#### *Acknowledgments.*

The authors gratefully acknowledge the considerable help given them by Dr. A. G. Quarrell, and also express their thanks to Mr. G. A. de Belin and Mr. H. T. Protheroe for the helpful interest that they have taken in the work. The investigation was undertaken

for the Hair-Line Crack Sub-Committee of the Alloy Steels Research Committee, and, although the authors are entirely responsible for the views expressed above, they greatly benefited by the helpful and constructive criticism of the Members of the Hair-Line Crack Sub-Committee.

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[This paper was discussed jointly with the preceding one by Professor J. H. Andrew, H. Lee and A. G. Quarrell on "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys" and the following one by Professor J. H. Andrew, A. K. Bose, H. Lee and A. G. Quarrell on "The Formation of Hair-Line Cracks.—Part II."]

# THE FORMATION OF HAIR-LINE CRACKS.—PART II.\*

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(Figs. 18 to 47 = Plates IX. to XVI.)

*Paper No. 6/1942 of the Alloy Steels Research Committee (submitted  
by the Hair-Line Crack Sub-Committee).*

## SUMMARY.

The work described in Part I. is confirmed and greatly extended. Typical hair-line cracks were produced in large specimens which had been air-cooled after hydrogen-soaking, but the bulk of the work was carried out on small specimens which had been hydrogen-treated and quenched. The evolution of gas from such specimens, both at room temperature and on heating, was investigated and the nature of the incubation period explained.

The results obtained lead to the following conclusions : (i) Hydrogen is the fundamental cause of hair-line cracks. (ii) The hydrogen which subsequently causes cracks is not in solid solution, but, for a time, is held in the form of a hydrogen-rich constituent which is formed on rapid cooling through the  $\gamma$ - $\alpha$  change. (iii) Breakdown of the constituent releases hydrogen, some of which diffuses into voids and builds up a disruptive pressure. (iv) In addition to hydrogen, the cracks contain methane, even at room temperature, and the presence of this methane is the cause of some of the difficulties encountered in the industrial prevention of hair-line cracks. (v) The influence of composition upon the susceptibility of a given steel to hair-crack formation is explained by the effect of composition upon the stability of the resulting hydrogen-rich constituent. (vi) Finally, once the constituent has been formed, its breakdown at low temperature must lead to hair-crack formation; on the other hand, hair-line cracks will not result if the breakdown of the constituent can be brought about at a sufficiently high temperature.

## INTRODUCTION.

It was shown in Part I.<sup>(1)</sup> that internal defects similar to hair-line cracks could be produced by soaking steel specimens in hydrogen at a high temperature, followed by rapid cooling and ageing, thus confirming the work of Musatti and Reggiori.<sup>(2)</sup> Similar treatment in nitrogen or a vacuum did not produce any such defects. Furthermore, evidence was obtained that, immediately after formation, the cracks contained hydrogen. Accordingly, the work to be

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reported here is mainly concerned with the rôle of hydrogen in the production of hair-line cracks.

TABLE I.—*Composition of the Steels Employed.*

Steel.	C. %.	Si. %.	Mn. %.	P. %.	S. %.	Ni. %.	Cr. %.	Other Elements. %.
<i>F1</i>	0.28	0.19	0.26	0.025	0.018	3.13	1.35	0.31 Mo
<i>F4</i>	0.61	0.20	0.80	0.04	0.04	...	...	...
<i>F5</i>	0.22	0.16	0.57	0.039	0.042	3.80	...	...
<i>4S11</i>	0.33	0.22	0.57	0.027	0.034	3.18	0.70	0.23 Mo
<i>C8</i>	0.27	0.05	0.69	0.017	0.024	3.90	1.34	0.54 Mo
<i>C9</i>	0.30	0.25	0.61	0.035	0.030	4.04	1.35	0.51 Mo
<i>C10</i>	0.20	0.85	0.70	0.029	0.024	3.98	1.45	0.54 Mo
<i>C11</i>	0.34	1.88	0.70	0.012	0.028	3.90	1.44	0.54 Mo
<i>F13</i>	0.24	0.19	1.03	0.02	0.04	2.34	...	0.74 V
<i>F23</i>	0.33	0.06	0.60	0.012	0.035	4.04	...	0.30 Ta
<i>F24</i>	0.53	0.44	0.87	0.034	0.018	3.93	...	0.27 Ti
<i>F26</i>	0.61	0.21	0.37	0.024	0.011	...	...	...
<i>S65</i>	0.29	0.22	0.45	0.031	0.028	2.98	1.34	0.34 Mo

As already reported in Part I., steel *F1* was a high-frequency melt. Steel *4S11* was made in the acid open-hearth furnace and was supplied by the English Steel Corporation, Ltd., through the kindness of Mr. H. H. Burton, in the form of  $1\frac{3}{4}$ -in. dia. rolled bar. The steel was treated by Mr. Burton to render it "unsusceptible to hair-line cracks," and was tested at the works and found to be free from the defect. Steel *F26* was a commercial medium-carbon steel, purchased in the form of 3-in. dia. bar. All the other steels were crucible melts made in the Metallurgical Department, Sheffield University, 50-lb. charges being cast into 3-in. square ingots and subsequently rolled into  $1\frac{3}{4}$ -in. round bars.

The only steels which could be sawn in the as-quenched condition were *F1* and *F5*. Neither showed cracks when sectioned immediately after quenching.

Control specimens of all steels were examined in the as-received condition by deep etching and by the magnetic crack detector. All such specimens were found to be free from cracks.

Three sizes of specimen were employed :

A.— $1\frac{3}{4}$  in. in dia.  $\times$   $1\frac{1}{2}$  in. long.

B.— $\frac{7}{8}$  in. in dia.  $\times$  3 in. long.

C.— $1\frac{3}{4}$  in. in dia.  $\times$  2 in. long with an axial hole  $\frac{5}{16}$  in. in dia. and  $\frac{1}{2}$  in. deep.

#### *Standard Hydrogen Treatment.*

Unless otherwise specified in the text, all specimens received 90 hr. treatment in hydrogen at 1200° C. followed by water-quenching.

In what follows, for example, the description *4S11A* will mean

that the specimen was of 4S11 composition and of size  $1\frac{3}{4}$  in. in dia.  $\times$   $1\frac{1}{2}$  in. long, and had received the standard hydrogen treatment followed by water-quenching.

### *Examination for Cracks.*

The method of examination for cracks adopted as standard throughout the work to be described consisted in deep-etching a complete longitudinal section and a half transverse section in boiling hydrochloric acid for 2 hr. This method showed up all the cracks which were revealed by the magnetic crack detector, and, in addition, frequently exposed narrower cracks which were too fine for detection by the magnetic method. This is well illustrated by Figs. 18 and 19, which show the appearance of the same surface after magnetic testing and deep-etching, respectively. The distribution of cracks in this specimen of 4S11 steel is typical of all the alloy steels which were subjected to the hydrogen treatment. The cracks are radial with respect to the centre of the specimen in both longitudinal and transverse sections. With plain carbon steel F26, however, the cracks were not radial, but were distributed more uniformly throughout the specimen, some of them being very deep-seated. Fig. 20 shows the appearance of such a specimen after magnetic testing, and Fig. 21 the same surface after deep-etching. Thus, here again, deep etching is more effective in showing up the fine cracks and, in addition, the macro-structure of the specimen is revealed, showing that some of the cracks are intercrystalline and others transcrystalline. The general tendency seems to be for the larger cracks to be intercrystalline, whilst the smaller ones are transcrystalline. When the specimen of Figs. 20 and 21 was fractured, the flakes exposed had the appearance of cleavage planes, as shown in Fig. 22.

All the results obtained are in agreement with the view that the distribution, but not the occurrence, of hair-line cracks in hydrogen-treated specimens is governed by the stresses resulting from the quenching treatment. Thus, as shown in Part I., the crack zone tends to conform to the shape of the specimen, but probably the best evidence is that afforded by Fig. 23. In this specimen of steel F4, severe quenching cracks almost completely divided the specimen into four parts, each of which behaved, so far as hair-cracks were concerned, as a separate specimen.

### EVOLUTION OF GAS AT ROOM TEMPERATURE.—INCUBATION.

In Part I. it was shown that time must elapse after quenching before cracks were developed in hydrogen-treated specimens, an observation which was in agreement with the work of Klausting.<sup>3)</sup> At that time the nature of the incubation period was not known, but because of the hydrogen treatment which the specimens had received, and the evidence which had been obtained in support of

the view that the cracks contained hydrogen immediately after formation, it seemed probable that the incubation might be connected with loss of hydrogen from the specimen. The following experiment was therefore carried out. Hydrogen-treated specimens were quenched and enclosed in a vacuum system. The gas evolved from the specimens was collected, measured and analysed. The apparatus previously used for solubility determinations, and already described,<sup>(4)</sup> was adapted for the present purpose by the addition of a Toepler pump for taking gas samples.

Immediately after quenching, the specimen was thoroughly washed with acetone and dried with as little delay as possible. The system was thoroughly evacuated after the specimen had been

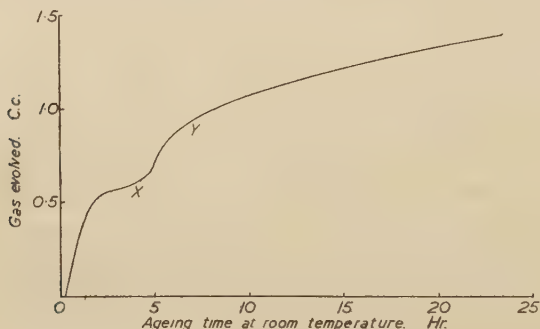


FIG. 1.—Evolution at Room Temperature from *F1B*.

introduced and the first manometer reading taken within 12 min. of quenching. As reported previously, the manometer employed was of the gas-analysis type, so that pressure readings could be taken at a known constant volume. This facilitated plotting the results as curves showing the volume of gas evolved against time.

Figs. 1 and 2 show the evolution of gas at atmospheric temperature for specimens *F1B* and *F5B*, respectively. The rate of evolution remains approximately constant for the first  $1\frac{1}{2}$  hr., and then gradually falls off during the next 2 hr. or so. Beginning at a point *X* and ending approximately at the point *Y*, marked on both figures, there is a sudden evolution of gas from the specimen. For *F1B* this evolution begins at 4 hr. and ends 7 hr. after quenching, whilst for *F5B* the corresponding times are  $3\frac{1}{2}$  and 6 hr.

Similar experiments were carried out with specimens *F1A* and *F5A*, and the results are shown in Fig. 3. In both cases the sudden evolution was much more marked and occurred after longer times than with smaller specimens of the same steel. With *F1A* the evolution of gas during the first 35 hr. totalled 2.5 c.c., whilst during the next half-hour no less than 3 c.c. of gas were evolved. The total gas obtained during the 48 hr. immediately after quenching

was 7 c.c. (equivalent to 1.51 c.c. per 100 g.). In the case of *F5A* the marked evolution of gas began at 31 hr.

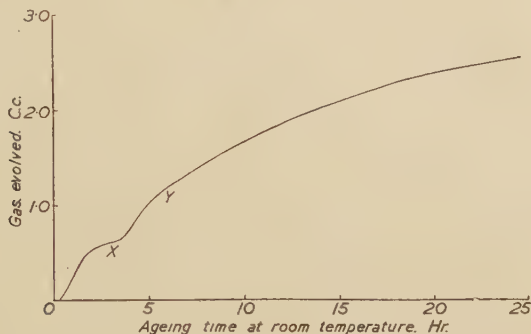


FIG. 2.—Evolution at Room Temperature from *F5B*.

After the marked evolution had taken place, the rate of evolution gradually diminished. No further pressure changes could be observed on the manometer three or four days after quenching, the actual time depending upon the size of the specimen. It is

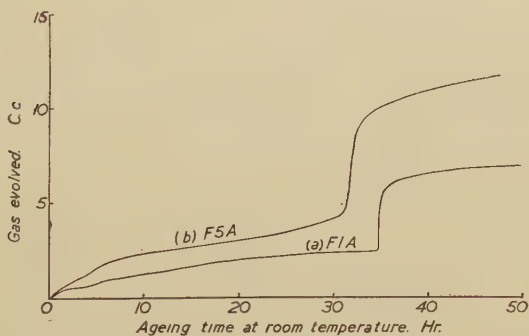


FIG. 3.—Evolution at Room Temperature from *F1A* and *F5A*.

noteworthy that, for specimens of the same size, steel *F5* gave off more gas at room temperature than *F1* did; in the first 48 hr. after quenching, 11.7 c.c. of gas were collected from *F5A*, as against only 7 c.c. from *F1A*. A similar difference was observed with the smaller specimens, and with both steels less gas was evolved per 100 g. of metal from the smaller specimens.

Analysis of the gas was carried out in a Bone and Wheeler apparatus, and the results are given in Table II.

The results quoted for *F1A* have also been calculated in terms

TABLE II.—*Evolution at Room Temperature.*

Specimen.	Volume of Gas Evolved.	Composition of Gas Evolved.						Gas Evolved in 1st 48 hr. C.c. per 100 g.
		H <sub>2</sub> . %.	CH <sub>4</sub> . %.	CO. %.	CO <sub>2</sub> . %.	O <sub>2</sub> . %.	N <sub>2</sub> . %.	
F1B	1st 24 hr. 1.4 c.c.	81.6	1.7	2.24	3.4	4.6	6.46	0.91
	2nd 24 hr. 0.7 c.c.	85.7	2.1	1.90	3.1	2.6	4.60	
F5B	1st 48 hr. 2.5 c.c.	88.4	1.8	1.53	1.36	0.28	6.62	1.04
F5A	1st 24 hr. 3.4 c.c.	84.5	3.9	3.8	0.52	0.28	7.0	2.52
	2nd 24 hr. 8.3 c.c.	87.1	3.25	2.78	0.92	0.42	5.49	
F1A	1st 48 hr. 7.0 c.c.	88.5	4.5	0.48	0.29	0.19	6.04	1.51

of percentage by weight of the original steel : Hydrogen, 0.00012%; methane, 0.00005%; carbon monoxide, 0.000009%; carbon dioxide, 0.000008%; oxygen, 0.000004%; and nitrogen, 0.00011%.

It will be seen from Table II. that in all cases the gas evolved consisted of at least 80% hydrogen. It is probable that the presence of nitrogen in the gas was largely due to the fact that nitrogen was passed into the furnace tube for a period of about 5 min. in order to replace the hydrogen atmosphere immediately before quenching the specimen. The oxygen figures for the first two samples in

Table II. are rather high, and it is thought that these results may be in error, owing to the small amount of gas available for the analysis.

In order to determine whether the sudden evolution of gas from quenched specimens was associated with hair-line crack formation, one specimen of F1B was sectioned 4 hr. after quenching, that is, immediately before the sudden evolution of gas would have occurred. This specimen showed no hair-line cracks (Fig. 24 (a)), but a similar specimen which had been quenched at the same time and sectioned 7 hr. after quenching, was found to be full of cracks (Fig. 24 (b)).

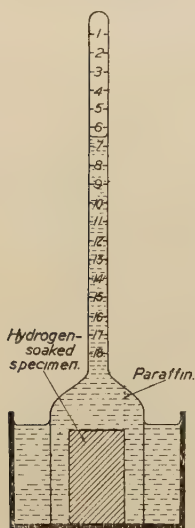


FIG. 4.—Apparatus for Determining Gas Evolution at Room Temperature.

It has been shown that with larger specimens of the same steel the sudden evolution of gas occurred 35 hr. after quenching. Further, the time taken for sawing such specimens in the quenched state was about  $1\frac{1}{2}$  hr. Accordingly, the sectioning of the specimen F1A was commenced at 32 hr., and the etching section is shown in Fig. 25; the lower half of the longitudinal section is completely free from cracks, but the upper half, which was the last portion of this section to be sawn, contains a few. The transverse section, on the other hand, has a



well-developed system of hair-line cracks, and it is significant that this section was cut immediately after the longitudinal section had been completed.

These experiments proved that crack formation is intimately connected with the evolution of gas at room temperature, and it was therefore desirable to extend this type of examination to as many specimens as possible. To do this, a new method of following the gas evolution at room temperature was devised. A glass tube of uniform bore, closed at one end, was joined to the stem of a wide-mouthed glass vessel, giving a construction resembling an inverted thistle funnel (Fig. 4). The glass tube, which was graduated in cubic centimetres, was filled with coloured paraffin and immersed in the same liquid, precautions being taken that no air bubble was trapped in the stem. The hydrogen-treated and water-quenched specimen was then placed under the funnel and the gas given off by the specimen collected in the graduated stem, where its volume could be measured directly. This device had the advantage that the quenched specimen could be placed under paraffin within a minute of quenching, and therefore even less gas was lost than with the vacuum method. Furthermore, owing to the simplicity of the design, it was possible to have several experiments running simultaneously under strictly comparable conditions. On the other hand, it was not possible to analyse the gas evolved from the specimen.

The type of gas evolution curve obtained with the paraffin apparatus was similar to that yielded by the vacuum system. At first, gas bubbles came off rapidly from the specimen, and then at an ever diminishing rate until the end of the incubation period. At this point, the sudden increase in the rate of evolution was most spectacular, and it was possible to see the gas bubbles leaving the surface of the specimen in a continuous stream. In extreme cases as much as 8.0 c.c. of gas were evolved in 5 min. from a specimen weighing 600 g.

Many experiments were carried out with the vacuum system and it was found that in all cases, irrespective of the composition of the steel, the gas evolved at room temperature consisted of 80–90% of hydrogen.

The four steels C8, C9, C10 and C11, with silicon contents of 0.05, 0.25, 0.85 and 1.88%, respectively, were hydrogen-treated and quenched, and the gas evolution at room temperature was followed in the paraffin apparatus. The volumes of gas evolved at room temperature in the first week after quenching differed only slightly from specimen to specimen, being 4.23, 4.38, 4.34 and 4.63 c.c. per 100 g. for C8, C9, C10 and C11, respectively, using specimens of type A. The shapes of the evolution curves (Fig. 5) were very different, however. Thus, C8 and C9 gave a series of small steps rather than a sudden evolution, whilst C10 and C11 showed marked incubation at 58 and 9 hr., respectively.

Since C10 and C11 showed a well-marked incubation, comparison was made between these steels when soaking was carried out at 1150° and 1200° C., respectively. The results recorded in Table III. were obtained. Thus, in the same steel, the incubation period is the

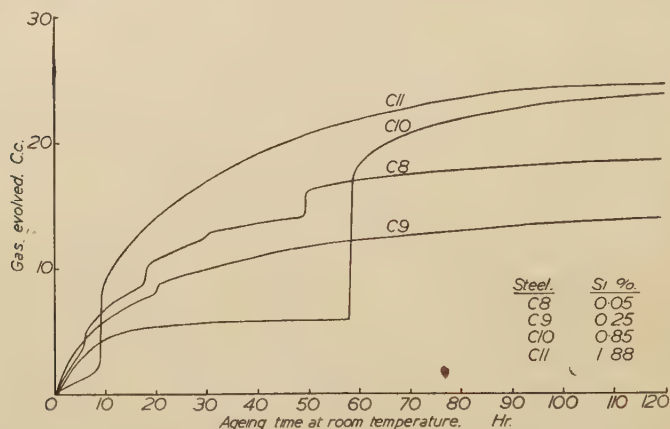


FIG. 5.—Effect of Silicon on Gas Evolution.

shorter the greater the volume of gas evolved at room temperature. It would also appear that the higher the silicon content the shorter is the incubation period, although it must be borne in mind that the carbon content of C10 is only 0.20%, as against 0.34% for C11.

TABLE III.—Effect of Soaking Temperature.

			Soaking at—	
			1150° C.	1200° C.
C10.	Incubation period. Hr.	.	170	58
	Gas evolved. C.c. per 100 g.	.	2.29	4.34
C11.	Incubation period. Hr.	.	72	9
	Gas evolved. C.c. per 100 g.	.	2.46	4.63

Confirmation that the evolution curve for certain steels showed a number of small steps rather than a sudden evolution was obtained during experiments carried out with steel 4S11. In this series, the time of soaking at 1200° C. for specimens of type C was varied, and in general the evolution curve was smooth or showed only a few small steps, or tended towards a gradual increase in the rate of evolution after a certain length of time. In three

cases a sudden evolution was observed, see Table IV. These results are in keeping with the authors' view that the shorter the incubation period the greater is the volume of gas evolved at room temperature.

TABLE IV.—*Evolution at Room Temperature from 4S11.*

Time of Soaking. Hr.	Incubation Period.	Gas Evolved. C.c. per 100 g.
142	3.25 hr.	6.71
187	7-18 hr.	5.40
70	11 days	3.88

With steel *F26* the incubation period of  $2\frac{1}{2}$  hr. was well-marked and reproducible. Furthermore, the sudden evolution was more pronounced than with any other steel examined. It was therefore decided to employ this steel to investigate the effect of heating during the incubation period. After a number of tests, an oil was obtained which could be heated to  $150^{\circ}$  C. without giving off vapour. This oil was used to replace the paraffin, and immediately after hydrogen treatment and quenching, a specimen, *F26A*, was placed in the evolution apparatus filled with the oil. The gas-evolution curve on heating to  $150^{\circ}$  C. was then taken, and is shown in Fig. 6; it may be compared with the normal curve obtained at room temperature (Fig. 7). On heating, the incubation period occurred after only 10 min., as compared with  $2\frac{1}{2}$  hr. at room temperature. On the other hand, the volume of gas evolved before the

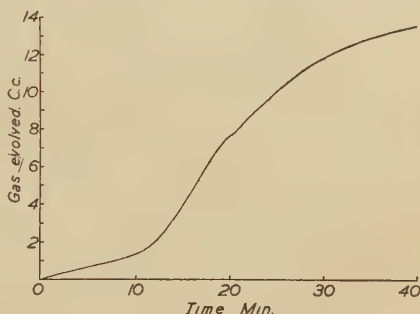


FIG. 6.—Evolution from *F26* on Heating to  $150^{\circ}$  C.

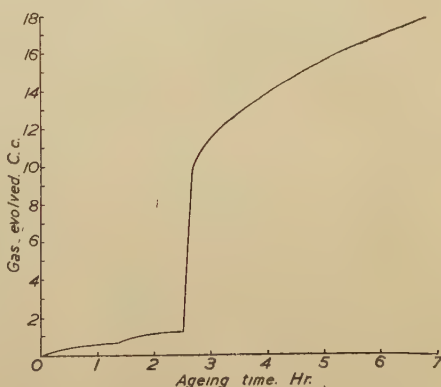


FIG. 7.—Evolution at Room Temperature from *F26*.

sudden evolution was in each case about 1.5 c.c. per 100 g. This rather suggested that, given the same hydrogen treatment, specimens of the same steel must lose a certain critical amount of gas before the sudden evolution could take place. General confirmation of this hypothesis, based on the results obtained with alloy steels, was not possible, owing to local segregation in these steels, but in one other case, at least, supporting evidence was obtained. With specimens of steel *C10*, of size *A*, soaked in hydrogen at 1200° and 1150° C., respectively, the volumes of gas evolved during incubation were 1.21 and 1.31 c.c. per 100 g., respectively, although the corresponding incubation periods were very different, being 58 hr. and 7 days.

In the first experiments on gas evolution at room temperature specimens which had shown a marked incubation formed cracks that were radially distributed. As this radial distribution was almost certainly due to residual stresses in the quenched specimens, the argument might have been put forward that the sudden evolution of gas was to be attributed to an instantaneous release of these stresses. As described above, however, the most marked incubation was observed with steel *F26*, in which the cracks showed no radial distribution, but were randomly disposed throughout the section, some being very deep-seated (Fig. 21). The cracks in steel *F26* were straight, and the flakes which appeared in fractured surfaces had the appearance of cleavage planes. As shown in Fig. 21, the grain size of this steel after prolonged soaking at 1200° C. is very large, and it may well be that the "flakes" are indeed cleavage planes or crystal faces.

TABLE V.—*Hydrogen-Treated Tantalum Steel F23.*

Soaking time. Hr. . . . .	6	17	142	260
Incubation . . . . .	Yes	Yes	No	No
Gas evolved at room temp. C.c. per 100 g. in 10 days . . . . .	4.6	2.7	2.0	2.3
Total length of cracks in longitudinal section. Mm. . . . .	204	129	109	Dots
Length of cracks per c.c. per 100 g. at room temp. Mm. . . . .	42	48	54	...

Specimens of *F23*, machined to size *A*, were soaked in hydrogen at 1200° C. for 6, 17, 142 and 260 hr., respectively. The specimens soaked for 6 and 17 hr. showed marked incubation, but no sudden evolution at room temperature was observed with those soaked for longer times. One of the most remarkable features of these experiments with the tantalum steel was that the longer the time of soaking the less was the gas evolved at room temperature. Furthermore, as the time of soaking in hydrogen was increased the cracks became shorter, until with 260 hr. the cracks were virtually dots. Even with the first three specimens, relatively few cracks were

formed, and, as these were remarkably straight, it was possible to measure the total length of cracks which appeared in the longitudinal section; in the first three specimens the total length of cracks in the longitudinal section for each cubic centimetre of gas evolved per 100 g. of steel at room temperature was of the same order, as shown in Table V.—this in spite of the considerable difference in the amount of gas evolved at room temperature.

#### GAS EVOLUTION ON HEATING AGED SPECIMENS.

Besides determining the rate of gas evolution at room temperature, it was considered desirable to investigate the effect of heating upon the loss of hydrogen from quenched specimens. In the first experiments, specimens *F1B* were hydrogen-treated and quenched, and placed in the Pythagoras tube of the vacuum furnace, which was then evacuated and isolated from the vacuum pump by means of a high-vacuum tap. The specimen was heated to  $1100^{\circ}\text{C}$ . in  $2\frac{1}{2}$  hr., and pressure readings were taken on the mercury manometer at  $50^{\circ}\text{C}$ . intervals. Fig. 8 (*a*) represents a typical result obtained on a specimen that had previously been allowed to age for 75 hr. at atmospheric temperature, during which period the hair-line cracks were formed; very little gas was evolved below  $300^{\circ}\text{C}$ . and the curve as a whole is very irregular, with a marked evolution above the change point. The specimen was originally considerably oxidised on the surface owing to quenching, and this oxide had not been removed before heating. Analysis of the gas collected showed that it consisted of 61.6% of carbon monoxide and only 29.8% of hydrogen (Table VI.). At the conclusion of the experiment it was seen that the oxide film on the specimen had been reduced, and it seemed probable that the irregular nature of the curve, Fig. 8 (*a*), was due to reaction between the oxidised surface, the carbon in the steel and the hydrogen.

To test this another specimen of the same steel was hydrogen-

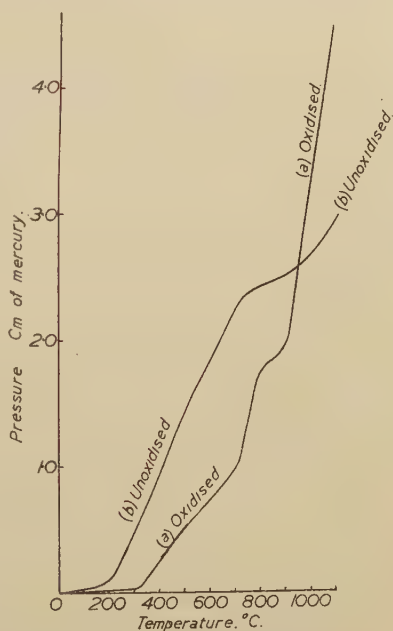


FIG. 8.—Evolution on Heating *F1B*,  
(*a*) oxidised, (*b*) unoxidised.



treated and quenched, and all traces of surface oxide were removed before heating in the vacuum furnace. In this case heating was commenced  $3\frac{1}{2}$  hr. after quenching, and, as shown in Fig. 8 (b), the evolution of gas became marked above  $150^{\circ}\text{C}$ . From about  $200^{\circ}\text{C}$ .

TABLE VI.—*Evolution from F1 on Heating.*

Specimen.	Composition of Gas.					
	H <sub>2</sub> . %.	CH <sub>4</sub> . %.	CO. %.	CO <sub>2</sub> . %.	O <sub>2</sub> . %.	N <sub>2</sub> . %.
F1B (oxidised)	29.8	1.47	61.6	2.35	0.42	4.36
F1B (oxides removed)	84.0	2.77	10.4	0.57	0.44	1.8

up to the  $\text{Ac}_1$  change the curve was almost linear, whilst between  $\text{Ac}_1$  and  $\text{Ac}_3$  the rate of evolution decreased, but increased once more after  $\text{Ac}_3$ , although this increase was much less marked than with the oxidised specimen previously examined. After cooling to room temperature, a sample of the gas was analysed and was found to consist of 84% of hydrogen.

The experience gained in these experiments showed that, not only was it necessary to remove all surface oxides, but also a more sensitive manometer was required before it would be possible to detect small changes in the rate of evolution of gas. Furthermore, the vacuum furnace was fitted with a Pythagoras tube which was too small for the examination of any but the smallest specimens. Accordingly, the apparatus was modified and fitted with a refractory tube which would take specimens up to 2 in. in dia., and a sensitive differential oil manometer was also incorporated. At the same time a Chromel-Alumel couple was fitted inside the tube, so that thermal curves of the specimen could be taken at the same time as the gas evolution was recorded.

After preliminary experiments with the modified apparatus, the following procedure was found satisfactory, and was adopted as standard for the rest of the work. While the normal heating curve of the specimen, type C, was being taken with the aid of a Tinsley vernier potentiometer, readings on the oil manometer were taken at one-minute intervals. Successive differences between the manometer readings were plotted against the corresponding temperatures to give a curve which showed the way in which the gas evolution varied with the temperature. For convenience, the thermal inverse-rate curve was plotted side by side with the evolution curve. The sensitivity of the oil manometer was such that a change in reading of 1.0 mm. corresponded to a gas evolution of 0.05 c.c. per 100 g. of metal when specimens  $1\frac{3}{4}$  in. in dia.  $\times$  2 in. long were employed. Heating to  $1000^{\circ}\text{C}$ . took place in  $1\frac{1}{2}$  hr., and the temperature was maintained at that value for a further 2 hr. The furnace was then allowed to cool down, and when

room temperature had been reached the manometer reading was taken to give the total volume of gas evolved from the specimen, and a sample of gas was collected for analysis.

As a considerable quantity of 4S11 steel, rolled and ground to  $1\frac{3}{4}$  in. in dia., had been kindly provided by Mr. Burton, this was selected for a comprehensive investigation of the effect of hydrogen treatment and quenching. As already mentioned, this steel had been treated to render it unsusceptible to hair-line cracks, and the absence of cracks in the steel as received was confirmed in the laboratory by deep-etching and magnetic testing a number of sections. It was found that when specimens of 4S11 were hydrogen-treated in the as-received condition and then quenched, surface cracks were frequently observed which made any comparison difficult. Furthermore, the gas evolved on heating such specimens after hydrogen treatment contained a relatively large amount of nitrogen and carbon monoxide. A specimen was, therefore, heated *in vacuo* in the as-received condition to  $1000^{\circ}$  C. for 5 hr.; 2.7 c.c. of gas per 100 g. were evolved of the following composition: Hydrogen, 25%; methane, 14.7%; nitrogen, 37.2%; and carbon monoxide, 21.0% by volume. As it seemed likely that the high nitrogen content might be a contributory factor in the formation of the apparent quenching cracks, specimens were given a preliminary vacuum treatment before being soaked in hydrogen. The vacuum treatment consisted in heating to  $1000^{\circ}$  C. for 5 hr. and slowly cooling to room temperature, the furnace tube being continuously evacuated by means of a two-stage mercury diffusion pump, backed by a rotary oil pump. When the preliminary vacuum treatment was given to specimens of 4S11 no surface cracks appeared, and, in addition, the hair-line cracks observed were far more numerous.

A series of experiments was carried out with steel 4S11, and the effect of different times of soaking in hydrogen at  $1200^{\circ}$  C. was investigated, the preliminary vacuum treatment being given in all cases. Two specimens were soaked in hydrogen and quenched together; one was heated for evolution immediately after quenching, whilst the other was aged in paraffin at room temperature for one or two weeks before the evolution curve was taken. For the specimens aged before heating, no consistent relationship between the time of soaking in hydrogen and (i) the volume of gas evolved at room temperature, (ii) the volume of hydrogen evolved on heating, or (iii) the sum of (i) and (ii) was found.

In general, the volume of gas evolved at room temperature was of the order of 3.5 c.c. per 100 g., but where there was a marked evolution at room temperature corresponding to an incubation, this figure was increased to as much as 6.7 c.c. per 100 g. in a period of a week; of these, 1.6 c.c. per 100 g. was evolved in 10 min. at the time of incubation. As might be expected, when there was such a marked evolution at room temperature, there was a corresponding diminution in the gas evolved on subsequent heating.

The sum of the volumes of hydrogen evolved from the specimen at room temperature and on heating varied from 5.5 to 9.0 c.c. per 100 g., but there was no systematic variation with the time of soaking.

#### GAS EVOLUTION ON HEATING IMMEDIATELY AFTER QUENCHING.

When hydrogen-treated specimens were heated for evolution immediately after quenching, the surface oxides being removed in all cases, very little variation was observed in the total gas evolved. Thus, for all specimens, the total volume of gas was between 7.3 and 8.0 c.c. per 100 g., although the soaking time was varied from 17 to 260 hr. As the gas contained a variable amount of carbon monoxide, the results were expressed as "total hydrogen." This term is used to indicate the sum of the hydrogen content of the gas plus the hydrogen equivalent of the methane. Expressed in this manner, the results showed a more marked difference with time of soaking. The results are summarised in Table VII.

TABLE VII.—*Hydrogen-Treated 4S11, Unaged.*

Volumes in c.c. per 100 g.

Soaking Time. Hr.	Total Gas.	Carbon Monoxide.	Hydrogen.	Methane.	Total Hydrogen.
6	Gas sample accidentally destroyed.				
17	7.29	1.51	5.1	0.22	5.54
70	7.48	0.81	6.02	0.31	6.64
142	7.98	0.84	6.43	0.53	7.49
186	7.95	0.41	6.24	0.72	7.68
190	7.67	0.24	6.74	0.28	7.30
260	7.69	0.77	6.38	0.23	6.84

Before considering these results in detail, it will be convenient to consider some of the limitations of the method employed for evaluating the hydrogen contents of the specimens. It was shown above that the presence of a surface oxide film on the specimen could cause abnormally large evolutions of carbon monoxide at high temperatures, and it is reasonable to suppose that a similar effect would be caused by oxide inclusions in the steel. Some of the oxide inclusions will be removed during the vacuum treatment, and also progressively during the soaking in hydrogen. This view is supported by the general trend of the carbon monoxide values reported in Table VII.

During the determination of hydrogen by heating, reactions will occur which involve carbon, hydrogen and oxygen, the main products of the reactions being carbon monoxide, methane and water vapour. Any hydrogen combined as water vapour cannot

be estimated, and is therefore a total loss. It is clear that the presence of oxygen, whether as surface oxides or inclusions, will have an important bearing on the hydrogen thus lost, and the total hydrogen figures will be affected by any irregularities in the oxide content of the steel specimen.

In addition, a period of approximately one hour elapsed between quenching and heating for evolution. During this time the oxide was removed from the surface, and an unknown quantity of hydrogen escaped into the atmosphere and was not collected. In the case of specimens which were quenched at the same time as those for immediate evolution, but placed under paraffin, the amount of gas collected in the first hour varied from 0.25 to 0.50 c.c. per 100 g. Thus, this source of inaccuracy alone would explain a deviation in the total hydrogen figures of 0.25 c.c. per 100 g., and it is estimated that the total hydrogen figures are reproducible to within 0.5 c.c. per 100 g.

The results given in Table VII. thus indicate an increase in total hydrogen up to a soaking time of 142 hr., after which there is little change, although the specimen soaked for 260 hr. shows a reduction. This is almost certainly due to the extensive decarburisation which was apparent in the outer rim of the specimen.

#### COMPARISON OF AGED AND UNAGED SPECIMENS.

The main features of the rate-of-evolution/temperature curves obtained from specimens heated immediately after quenching were that (i) from room temperature the rate of evolution increased to a maximum in the neighbourhood of 300–350° C., followed by (ii) a second peak between 650° and 700° C., *i.e.*, just below the  $Ac_1$  point on the thermal curve, and (iii) a more uniform rate of evolution from the  $Ac_1$  point upwards. The evolution above the  $Ac_1$  change was usually small, but in the few cases where an abnormally large rate of evolution was observed in this temperature range, it was found that the carbon monoxide content of the gas was high. As explained above, this is attributed to the reaction between carbon and oxides in the steel.

When the corresponding aged specimens were examined, the evolution curves obtained were to some extent dependent upon whether or not a marked evolution of gas had previously occurred at room temperature. Thus, when the specimen showed a marked incubation period, the lower peak on the evolution curve in the neighbourhood of 300–350° C. was almost entirely absent, but when no such marked incubation took place this peak persisted, although much smaller than with the corresponding unaged specimens. The second peak at about 650° C. was, in general, smaller in aged than unaged specimens, but no effect which could be attributed to incubation was observed.

Typical curves are shown in Figs. 9 to 11. In each case the



broken curve refers to aged specimens, whilst the full line represents the evolution curve of the corresponding unaged sample. Figs. 10 and 11 were obtained from specimens of steel 4S11 soaked for 142 and 70 hr., respectively, and the corresponding incubation periods obtained from the specimens aged under paraffin were  $3\frac{1}{4}$  hr. and 11 days. Fig. 9 gives the curves for specimens which were soaked in hydrogen for 6 hr., but no incubation was observed during the ageing period.

With very short times of soaking the lower peak seemed to have a number of smaller maxima superimposed upon it, and as the soaking time increased to 70 hr. or more the points fell much more closely on a smooth curve. Again, in general, the longer

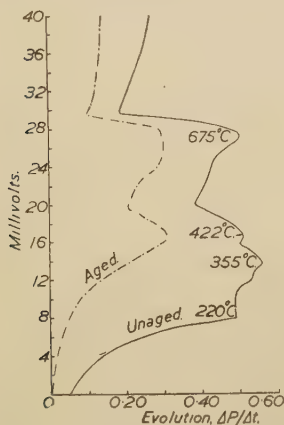


FIG. 9.—4S11C, soaked for 6 hr.

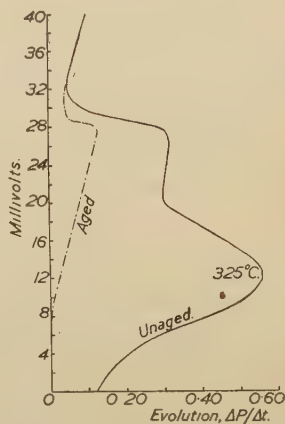


FIG. 10.—4S11C, soaked for 142 hr.

the soaking time the smaller was the *relative* magnitude of the 650° C. peak on the rate-of-evolution curve. Indeed, it would appear that the time of soaking has little effect upon the absolute magnitude of the upper peak, but the lower one increases with the time of soaking.

A direct comparison of the cracks obtained under different conditions is rendered difficult by the zig-zag nature of the cracks observed in steel 4S11; the following generalisations can be made, however: In specimens heated for evolution in the unaged condition, the number of cracks increased with the soaking time up to periods of 140 hr., and then remained appreciably constant. This is in keeping with the observed total hydrogen contents of the same specimens reported below.

The numbers of cracks occurring in specimens heated for evolution in the aged and unaged conditions were of the same order, but the appearances of the cracks differed according to the history



of the aged specimens. Thus, when the incubation period was marked, *i.e.*, when the cracks were definitely formed at room temperature, the cracks in the aged specimen were fine, and some were long, whereas in the corresponding unaged specimen, in which the cracks must have been formed on heating, they were relatively short and coarse. With specimens showing no incubation the cracks were very similar in aged and unaged specimens, being rather short and coarse, with the exception of a few long fine ones in the aged specimen.

With the unaged specimens, the cracks must have been formed

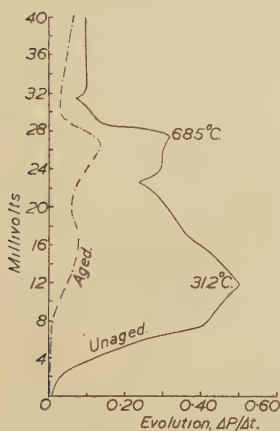


FIG. 11.—4S11C, soaked for 70 hr.

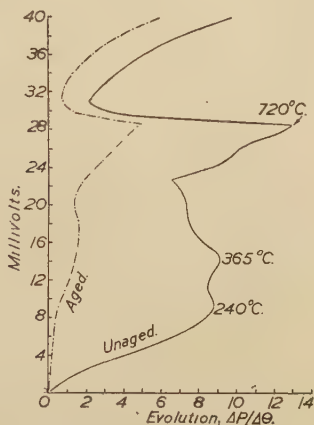


FIG. 12.—4S11C, soaked for 70 hr.; modified evolution curves.

during the heating for evolution, and the primary object of taking the evolution curve was to detect any sudden evolution of gas which might accompany crack formation on heating. Yet the evolution curves already presented showed no sudden evolutions, although there was in some cases a suggestion of a small peak at about 220° C. superimposed upon the main maximum in the neighborhood of 350° C. (Figs. 9 and 11).

The rate-of-evolution curves are subject to the criticism that the rate of heating of the specimen was far from uniform, especially from room temperature to about 300° C. This difficulty can be overcome, however, if the thermal inverse-rate curve is combined with the rate-of-evolution curve. Thus, by multiplying the time interval of the thermal curve by the rate-of-evolution at the same temperature, the result can be plotted as the increase in pressure per °C. rise in temperature, against temperature. The results shown in Fig. 11 are replotted in this manner to give Fig. 12. Certain of the features of these curves can be regarded as character-

istic of the evolution curves plotted in this manner.\* In addition to the two peaks at 350° and 650° C. which were observed on the ordinary evolution curve, the new curve for the unaged specimen also has a maximum at about 220° C. The curve of the aged specimen does not show this peak.

Since the object of this part of the work was to correlate the crack formation with the hydrogen evolution, the next step was to subtract the evolution curve of the aged specimen from that of the unaged, in order to obtain a "difference" curve which may be regarded as the evolution curve on heating for the hydrogen which disappears at room temperature during the ageing period. The difference curves for short-, medium- and long-time soaking (6, 70 and 142 hr., respectively) corresponding to Figs. 9 to 11 are

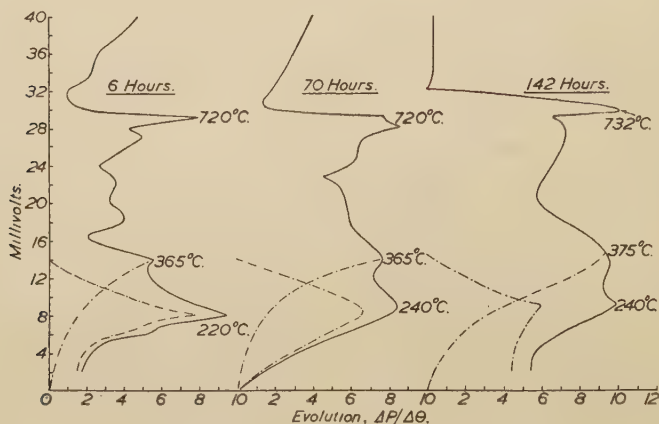


FIG. 13.—Difference Curves.

given in Fig. 13. The difference curve may be regarded as being made up of the separate peaks indicated by the broken lines.

As mentioned above, the original evolution curve for short-time soaking showed a number of subsidiary maxima, and these are more clearly distinguished on the difference curve. On the other hand, with a longer time of soaking, the curve is smooth except for the three main peaks at 220°, 350° and 650–700° C., respectively.

The interpretation of these difference curves is simplified by comparison with Fig. 14; the difference curve there shown was obtained from evolution experiments carried out on two crucible remelts of 4S11. Before casting, hydrogen was bubbled through

\* Strictly speaking, these are not true evolution curves, as they include effects due to the expansion of the gas with temperature. These effects will not change the main features of the curves, such as the peaks, and for convenience the term "evolution curve" is retained in the text.

the molten steel, which was then cast in a 3-in. square ingot, from which, when cold, standard specimens for evolution experiments were machined. The hydrogen contents of the two ingots were adjusted so that, from this point of view, the corresponding specimens were equivalent to aged and unaged quenched specimens. Neither of the cast specimens showed hair-line cracks, although one of the hydrogen contents was actually rather higher than were normally obtained in quenched specimens, the values being 9.80 and 3.05 c.c. per 100 g., respectively. Both specimens contained numerous blow-holes.

The chief difference between Fig. 14 and Fig. 13 is the absence of the 220° C. peak from the difference curve of the cast specimen. There are peaks at 310° and 460° C., but the peak at 650–700° C. is smaller than that in the quenched specimens. It seems reasonable to suppose that the 220° C. peak is intimately connected with hair-crack formation, but before this argument can be developed it is desirable to consider the factors which can influence the evolution on heating. These factors are :

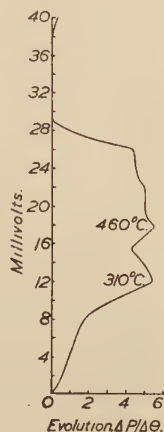


FIG. 14.—Difference Curve for Remelted 4S11.

(1) *Rate of Diffusion.*—This increases with temperature, and there is some evidence <sup>(5)</sup> for a marked increase at about 300° C. The rate of diffusion is greater in  $\alpha$ - than in  $\gamma$ -iron. <sup>(5)</sup>

(2) *Degree of Saturation with Hydrogen.*—This will affect the basic rate of evolution and, in addition, under the conditions of the present experiments, may cause slight variations in the position of the maximum rate of evolution on heating.

(3) *Changes in Structure.*

(4) *Release of Internal Strain.*

(5) *Sudden Release of Hydrogen due to Breakdown of a Hydrogen-Rich Constituent.*

(6) *Hydrogen Trapped in Voids.*—Compounds, such as methane, may be formed and decomposed at favourable temperatures, and their formation and decomposition will be reflected in the evolution curve.

Consider a steel specimen, containing hydrogen in solution, which is heated for evolution. The evolution of hydrogen at any temperature is determined by the rate of diffusion and the amount of hydrogen present. At low temperatures, and therefore low rates of diffusion, the rate of evolution will be low, but will increase with temperature. There will come a time, however, when, although the rate of diffusion is still increasing, the amount

of hydrogen evolved in a given time interval will be progressively smaller owing to diminution of the residual hydrogen content. Thus, the evolution curve must show a maximum, the exact temperature of which will, for given conditions of heating, vary with the initial hydrogen content of the specimen. It is believed that this peak is the one which occurs at 300–350° C. and which is observed in both quenched and cast specimens.

In Part I. it was shown that if a hydrogen-treated and quenched specimen was rapidly heated to 300° C., the metal in the immediate neighbourhood of the cracks was decarburised, and this was attributed to the action of hydrogen stored in the cracks. The decarburisation must result in the formation of methane. Additional evidence was afforded by experiments in which similar specimens were rapidly heated to 650° C. before sectioning; it was found that carbide globules were deposited round and along the cracks. It was further shown that these results were in complete agreement with those obtained during the determination of hydrogen solubility in a nickel steel. On this view, therefore, once the cracks have been formed they must be filled with hydrogen and, during heating for evolution, some methane will be formed, particularly in the neighbourhood of 300° C. Once this methane has been formed in the cracks, it cannot escape from the metal without first decomposing to give hydrogen. From 300° C. upwards the stability of methane decreases, and, as previously shown,<sup>(4)</sup> the decomposition of methane becomes extremely rapid beyond 650° C. These results were obtained from experiments carried out at normal pressures, and it is true that much higher pressures may exist within the cracks. Such high pressures, however, would favour the formation of methane at low temperatures, but, on the other hand, would tend to increase the temperature of rapid breakdown.

Bearing these considerations in mind, it is suggested that the peak just below the  $A_{c1}$  point is mainly to be attributed to the decomposition of methane formed within the cracks at lower temperatures. The increased rate of evolution is probably assisted by the process of changing from the  $\alpha$  to the  $\gamma$  lattice, and, in addition, the affinity of  $\gamma$ -iron for carbon may accelerate the decomposition of methane. When all the methane is decomposed, and when the thermal change is complete, the lower rate of diffusion of hydrogen in  $\gamma$ -iron results in a sudden drop in the rate of evolution, which accentuates the 700° C. maximum.

The subsidiary maximum at about 450° C. is probably connected with the release of internal strain which is known to occur at this temperature. In the difference curve for the cast steel, this peak appears rather more prominent than for the quenched specimens. It is believed that this is really due to the smaller "methane" peak. In this case the stored hydrogen is in blow-holes, and, therefore, is presumably at lower pressures than prevail



within the cracks of the quenched specimens. This will result in less methane being formed and in its earlier decomposition with increasing temperature. The resulting smaller methane peak causes the 450° C. maximum to appear relatively more important. In general, the 450° C. peak is more prominent with short- than with long-time soaking in hydrogen prior to quenching.

From the point of view of hair-line crack formation there can be little doubt that the most important feature of the evolution curves is the maximum at about 220° C. This peak is absent from the curves for the cast specimens in which no hair-line cracks developed, but is present in all the difference curves for quenched specimens which after heating showed hair-line cracks. In Part I. it was tentatively suggested that the formation of hair-line cracks might be intimately connected with the breakdown of a hydrogen-rich constituent. The results since obtained are in keeping with this view, and it is considered that the 220° C. peak is due to the breakdown of such a hydrogen-rich constituent. A fuller treatment must be postponed until the results of other experiments have been presented, but attention may be drawn to the fact that, as shown by the dotted lines in Fig. 13, the difference curves of the quenched steels are made up of a curve similar in general features to the curve of the cast steel, upon which is superimposed another curve extending from room temperature to about 360° C., with a maximum at 220° C.

#### MISCELLANEOUS EXPERIMENTS.

##### *Quenching to Different Temperatures.*

In Part I. a series of experiments was described in which steel F1 was used. After soaking in hydrogen at 1200° C. for 18 hr. the specimens were quenched in oil at 150° C., followed by a variety of subsequent treatments which were, in the main, based upon ageing at 150° C. In all cases the specimens were free from cracks. Similar experiments have now been carried out with steel 4S11, but with longer times of soaking in hydrogen (90 hr. at 1200° C.). After hydrogen-soaking, specimens of 4S11 were quenched in oil at 150° C., and it was found that immediately after quenching the temperature of the bath increased to 165° C. The oil was allowed to cool to 150° C. and the temperature was then maintained at this value to within 10° C. After 1 hr., one specimen was removed from the oil-bath and was allowed to age at room temperature for 72 hr. The other specimen was aged at 150° C. for 72 hr. After the ageing period, both specimens were softened by heating to 600° C., sectioned and examined in the usual manner. As shown in Fig. 27, the cracks in the specimen held at 150° C. for 1 hr. were numerous, and, although some were in the characteristic radial distribution, many were deep-seated and distributed at random. In the other specimen, aged for 72 hr. at 150° C., the



cracks were far fewer and all were near the surface. The experiment was repeated, but the hydrogen-soaked specimens of 4S11 were quenched into a lead-tin bath at 300° C. After this treatment both specimens had very bad surface cracks. The specimen held at 300° C. for 1 hr. and then aged at room temperature for 72 hr. showed relatively few cracks, which were randomly disposed at the centre of the specimen. The cracks themselves were short and wide, Fig. 26. In the specimen aged for 72 hr. at 300° C. no internal cracks were formed. Before sectioning these specimens, evolution curves on heating had been taken, and the difference curve is shown in Fig. 15. The total hydrogen contents of the two specimens were respectively 5.38 and 0.85 c.c. per 100 g. The difference curve has two very sharp peaks at 230° and 315° C. in addition to the usual methane peak at 700° C.

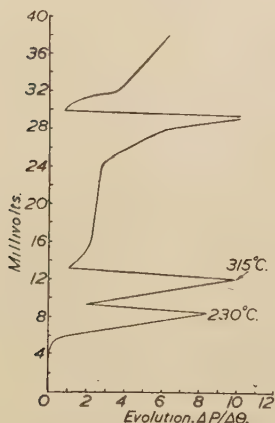


FIG. 15.—Difference Curve for 4S11, aged at 300° C.

#### *Heat Treatment of Hydrogen-Treated and Quenched Specimens.*

After receiving the standard hydrogen treatment followed by water-quenching, specimens F1A were immediately transferred to furnaces maintained at 300°, 475° and 650° C., respectively. After ageing for 50 hr. at the appropriate temperatures the specimens were water-quenched and sectioned without delay. Hair-line cracks were found in all cases, but, as shown in Fig. 29, as the temper-

ature of heat treatment was increased the cracks became fewer and generally shorter, and the specimen aged at 650° C. revealed only two long cracks.

In another series of experiments, separate specimens of F1A received one of the following heat treatments immediately after quenching: (a) 3 hr. at 200° C., (b) 3 hr. at 300° C., (c) 15 min. at 600° C. In all cases the specimens were then slowly cooled and were aged for a further period of 50 hr. at room temperature. Again, all specimens showed hair-line cracks, and, as illustrated in Fig. 30, they tended to be shorter than normal. In the specimen treated at 600° C. the cracks were definitely fewer in number and were virtually "dots."

As a result of general experience in the reheating of hydrogen-treated and quenched specimens of various steels, it may be said that the nature and number of cracks observed for a given steel depend upon the rate of heating. When the specimen is allowed to heat up with the furnace the cracks are as numerous as when

the specimen is allowed to age at room temperature, although the cracks are usually shorter and wider. If the freshly quenched specimen is placed in a furnace already at temperature, the cracks are fewer to an extent which depends upon the temperature, and again are shorter and wider.

*Influence of Quenching from Above and Below the  $A_{r1}$  Point.*

Specimens S65C and 4S11C were soaked in hydrogen at 1200° C. for 90 hr. and then allowed to cool to temperatures just above and just below the change point, respectively, before water-quenching. After the removal of surface oxides the specimens were vacuum-heated and the gas was collected. With both steels the specimens quenched above the change point showed hair-line cracks and also very bad surface cracks, but both defects were entirely absent from the specimens quenched below the change point. The results are summarised in Table VIII.

TABLE VIII.—*The Effect of Quenching through the  $A_{r1}$  Point.*

Steel.	$A_{r1}$ Point on A.C.	A.C. to and W.Q. from—	Time to Cool to Quenching Temp. Min.	Total Hydrogen Content. C.c. per 100 g.
S65	440° C.	490° C.	6	6.5
		385° C.	16	5.5
4S11	420° C.	520° C.	8	7.3
		385° C.	20	5.2

In the many experiments carried out on 4S11 water-quenched after soaking for various periods in hydrogen at 1200° C., the maximum amount of hydrogen retained was 7.7 c.c. per 100 g.; the specimen, therefore, lost very little hydrogen on cooling from 1200° to 520° C. Furthermore, although the amount of hydrogen lost when cooling through the change point was only of the order of 2.0 c.c. per 100 g., nevertheless this was very large compared with the hydrogen lost above the change point.

*Effect of Soaking in Ammonia.*

Vacuum-treated specimens 4S11A were soaked in ammonia at 1200° C. for 90 hr. and water-quenched. Simultaneously, similar specimens were soaked in hydrogen and water-quenched. In each case the specimen was aged in a vacuum system at room temperature and the gas evolved was measured and analysed. The specimens were then heated to 650° C. in the vacuum furnace until no further gas evolved. The results are given in Table IX. The ammonia-soaked specimen evolved surprisingly little gas at room temperature, but the total hydrogen evolved on heating at 650° C. was greater than that from the hydrogen-soaked specimen, owing to the

large proportion of methane evolved. In addition, much more nitrogen was evolved from the ammonia-treated specimen. The evolution at room temperature of the ammonia-treated specimen showed no marked incubation, but the curve followed the same general trend as that for the hydrogen-treated specimens, except that no further evolution of gas could be detected after two days.

TABLE IX.—*Comparison between Hydrogen and Ammonia Treatment.*

Gas evolved in c.c. per 100 g.

Temp. ° C.	Gas.	Hydrogen-Treated.	Ammonia-Treated.
20	Hydrogen	3.5	0.62
	Methane	0.26	0.14
	Nitrogen	0.02	0.06
	Total hydrogen	4.02	0.90
650	Hydrogen	3.58	3.90
	Methane	0.36	1.51
	Nitrogen	0.06	0.33
	Total hydrogen	4.30	6.92

The cracks in the ammonia-treated specimen were relatively few and coarse, and very similar to those obtained in specimens of the same steel which had been hydrogen-treated in the as-received condition. By comparison, the specimen which had been vacuum-treated and then hydrogen-treated for 90 hr. showed very numerous, fine and rather long cracks.

*Effect of Soaking Below the  $Ar_1$  Change Point.*

To decide whether it was necessary to soak the specimen in hydrogen above the  $Ac_1$  point in order to obtain hair-line cracks, specimens C9A were soaked for 140 hr. at 650° C. and water-quenched. No cracks were observed in either aged or unaged specimens.

As it was possible that the rate of dissociation of molecular hydrogen might be too low at 650° C. to give the necessary hydrogen content in the steel, the experiment was repeated with 4S11C, but soaking in ammonia at 600° C.; after soaking for 500 hr. one specimen was water-quenched whilst the other was heated in air to 800° C. in 15 min. and then quenched. No cracks were observed in either specimen, but both showed a pronounced nitrified rim about  $\frac{1}{8}$  in. thick. The bulk of the gas evolved on heating was nitrogen, but as a matter of interest the main results of the gas analysis are given in Table X. Apart from the nitrogen values, probably the most remarkable feature of these results is the high methane content compared with the hydrogen. On heating through the  $Ac_1$  in air, relatively little nitrogen is lost, but about 20% of the total hydrogen content is given off.

TABLE X.—*Ammonia Treatment Below Change Point.*

Gas evolved in c.c. per 100 g.

Gas.	Soaked in Ammonia at 600° C. and—	
	W.Q. from that Temperature.	Heated to 800° C. and W.Q.
Nitrogen . . .	137	131
Hydrogen . . .	2.2	0.85
Methane . . .	1.39	1.55
Total hydrogen .	4.98	3.95

*Treatment of Cast Specimens.*

Specimens of size *A* were machined from an ingot of steel 4S11, the specimens being taken from the same part of the ingot to ensure similar structures. One specimen was given a preliminary vacuum treatment and, together with the one in the as-received cast condition, was then soaked in hydrogen at 1200° C. for 90 hr. After water-quenching, the specimens were isolated in vacuum systems and the gas evolved during four days was collected and analysed. In order to extract the remaining gas, the specimens were then heated at 650° C. *in vacuo* until no further gas was evolved.

The vacuum-treated cast specimen gave a marked incubation at 22 hr., whilst the specimen hydrogen-treated in the as-received condition showed only a change in slope, illustrated in Fig. 16.

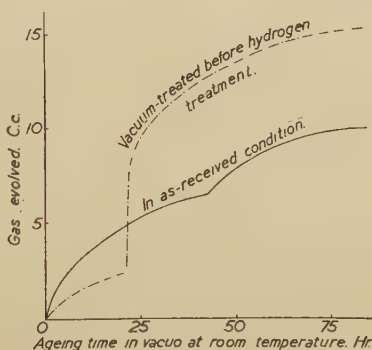


FIG. 16.—Effect of Vacuum Treatment on 4S11, as cast.

The analyses of the gases evolved at room temperature and on heating are given in Table XI. The gas given off by the specimen treated in the as-received condition contained a higher proportion of methane and of nitrogen than the vacuum-treated specimen. Furthermore, whereas the cracks in the vacuum-treated specimen were numerous and fine, and generally to be compared with those in forged specimens of the same steel, the cracks developed in the

as-received cast specimen were few and extremely coarse, and some extended to the surface of the specimen (Fig. 28).

TABLE XI.—*Effect of Vacuum Treatment upon Cast 4S11.*  
Gas evolved in c.c. per 100 g.

Temp. ° C.	Gas.	As Received.	Vacuum-Treated.
20	Hydrogen	1.25	2.89
	Methane	0.61	0.12
	Nitrogen	0.24	0.09
	Total hydrogen	2.47	3.13
650	Hydrogen	2.46	3.64
	Methane	1.47	0.37
	Nitrogen	0.17	0.14
	Total hydrogen	6.40	4.38

### *Melts Treated with Hydrogen.*

In connection with other work, a number of crucible remelts of 4S11 were made, suitable additions being made to counteract carbon pick-up. After killing with ferro-silicon and ferro-manganese, hydrogen was bubbled through the molten steel for 5 sec. at different rates. The steel was then cast into 3-in. square ingots, 22 in. long and air-cooled. When cold, a standard evolution specimen was machined from the sound bottom part of the ingot and the gas content determined within 48 hr. of casting. With eight melts the total hydrogen content was between the limits of 5.5 and 10.0 c.c. per 100 g., but in no case were hair-line cracks observed. As already reported, the difference evolution curves for two melts with high and low hydrogen contents, respectively, were similar to those obtained from quenched specimens, except that (i) the methane peak was smaller and (ii) the 220° C. peak was entirely absent.

## EFFECT OF ALLOYING ELEMENTS.

### *General.*

As shown in Figs. 20 and 21, the cracks in the plain carbon steel *F26* were not in the radial distribution usually observed in quenched specimens of alloy steels. On the other hand, in steel *F4*, which differed from *F26* only in that the manganese content was 0.80% instead of 0.37%, the cracks were far more numerous and for the most part confined to an outer annular zone, although the radial distribution was not marked. The distribution was obviously affected by the fact that four large cracks occurred in the section, so that from the point of view of hair-line crack formation, the specimen was divided into four smaller ones (Fig. 23).

The distribution of cracks in hydrogen-treated and quenched specimens of steel *F5*, containing 3.80% of nickel, was definitely



radial and the same applies to all specimens of alloy steels so far examined (Table I.).

To determine the effect of carbide- and hydride-forming elements upon hair-line crack formation, crucible melts of nickel-base steels *F13*, *F23* and *F24*, containing 0.74% of vanadium, 0.3% of tantalum, and 0.27% of titanium, respectively, were made and cast into 3-in. square ingots. A number of specimens of size *A* were machined from each ingot and the rest of the steel was forged to  $1\frac{3}{4}$  in. in dia. After the standard hydrogen treatment, hair-line cracks were produced in all three steels in the forged condition, whilst the vanadium steel showed cracks even in the cast state. Hydrogen treatment failed to produce cracks in the tantalum and titanium steels in the cast condition, but these steels were badly piped.

The cracks were more numerous in the nickel-chromium-molybdenum steels *F1*, *4S11* and *S65* than in the plain nickel steel. In *F1* the cracks were fine and straight, in *4S11* they were coarser and zig-zagged, whilst *S65* gave results about intermediate between them.

A series of steels, *C8*, *C9*, *C10* and *C11*, with nickel-chromium-molybdenum base and different silicon contents, was made, and specimens were examined after hydrogen treatment in both the as-cast and the forged conditions. As shown in Table I., the nickel, chromium and molybdenum contents of these steels were fairly constant, and, although the carbon content varied from 0.20 to 0.34%, the major difference between the steels was in the silicon content, which was 0.05, 0.25, 0.85 and 1.88% for *C8*, *C9*, *C10* and *C11*, respectively. Specimens *C8A* and *C9A*, hydrogen-treated in the as-cast condition, were quite free from hair-line cracks, but similar specimens of *C10* and *C11* had pronounced cracks. In the forged condition all specimens showed numerous hair-line cracks, their number and size increasing with the silicon content. Thus, the cracks in *C8* were, if anything, rather finer and fewer than normal, whereas those in *C11* were the worst yet obtained. All the cracks in *C8* and *C9* tended to be zig-zagged, whereas those in *C10* and *C11* were straighter and well-defined. *C10* and *C11* invariably showed a marked incubation at room temperature, but the corresponding evolution curves of *C8* and *C9* contained only a series of small steps (Fig. 5).

### *Effect of Carbon.*

In order to make possible a study of the effect of carbon upon the hair-line crack formation, Messrs. Hadfields, Ltd., through the courtesy of Mr. W. J. Dawson, kindly made and supplied five nickel-chromium-molybdenum steels with varying carbon contents. The steels were made in the high-frequency furnace, and were forged to  $1\frac{3}{4}$  in. in dia., each piece being about 18 in. long. The compositions were: Chromium, 1.2–1.4%; nickel, 3.2–3.3%;

molybdenum, 0.28–0.30%; manganese, 0.18–0.22%; and silicon, 0.23–0.42%; while the carbon contents were 0.08, 0.11, 0.20, 0.35 and 0.44% for *D1*, *D2*, *D3*, *D4* and *D5*, respectively.

Two specimens of size *C* were machined from each steel, and were soaked in hydrogen at 1200° C. for 90 hr. and water-quenched. One specimen of each composition was heated for evolution immediately, whilst the other was placed under paraffin and the gas evolution at room temperature was recorded. The results obtained are summarised in Table XII. The volumes of gas evolved at

TABLE XII.—*Effect of Carbon Content of Steel on Gas Evolution.*

Steel : Carbon. %.		<i>D1</i> . 0.08	<i>D2</i> . 0.11	<i>D3</i> . 0.20	<i>D4</i> . 0.35	<i>D5</i> . 0.44
Gas evolved at 20° C.	C.c. per					
100 g. in 7 days . . .		3.92	2.37	2.11	1.52	1.12
Total gas on heating.	C.c. per					
100 g. . . . .		7.06	7.62	8.37	8.59	8.36
Total hydrogen on heating.						
C.c. per 100 g. . . . .		6.63	7.06	7.98	7.35	7.19
Low-temperature evolution						
peak. ° C. . . . .		50	100	240	270	315

room temperature decreased with increasing carbon content. Furthermore, the combination evolution curves taken on heating showed a low-temperature evolution peak of the type already ascribed to the breakdown of a hydrogen-rich constituent, but the temperature of this peak increased with the carbon content of the steel. The total volume of hydrogen evolved during heating increased with the carbon content up to about 0.20%, but beyond that composition there was a falling-off in the total hydrogen collected. Comparison of the figures for total gas with those for total hydrogen reveals that steels *D4* and *D5* gave off relatively large amounts of carbon monoxide, as was confirmed by the analyses, and, as already pointed out, this must have been due to the presence in the steel of correspondingly large amounts of oxide, which in its turn would result in the loss of some hydrogen. In general, the size of the methane peak (650–700° C.) increased with the carbon content of the steel.

The specimens heated for evolution and those aged at room temperature were all sectioned and examined for hair-line cracks. In the aged specimens, which had to be softened by heating to 600° C. before sectioning, the cracks differed in appearance according to the carbon content. This is illustrated in Fig. 31; the cracks in *D1* and *D2* are short, numerous and fine, those in *D3* are longer than in *D1* and *D2*, but are still fine and numerous, whilst those in *D4* and *D5* are fewer and longer, and there are some very long ones in *D5*. In the specimens heated for evolution immediately

after quenching all the cracks were short, and there was practically no difference between the appearance of *D1* and *D2* in the aged and unaged conditions. In *D3*, however, although the cracks were as numerous in the unaged as in the aged specimen, they were rather shorter. In *D4* and *D5* this tendency was even more pronounced, but besides being shorter, the cracks were also fewer in the specimen heated immediately after quenching.

In view of the effect of heating immediately after quenching upon the cracks obtained in the steels of higher carbon content, the effect of controlled heat treatment was investigated. Since the uniform-temperature zone of the hydrogen soaking furnace was restricted to about 6 in., it was not advisable to soak more than four specimens of size *A* simultaneously. Accordingly, since *D1* and *D2* were of almost equal carbon contents and had been found to behave similarly, it was decided to use steels *D2*, *D3*, *D4* and *D5* for the experiment. Four specimens, one of each of these steels, were given the standard hydrogen treatment together, and immediately after quenching were transferred to an electric muffle controlled at 600° C. and already at that temperature. After holding at this temperature for 24 hr., the specimens were air-cooled, sectioned and examined for hair-line cracks. The experiment was repeated, but with the heat treatment at 200° C. instead of 600° C. The resulting sections, after deep-etching, are shown in Figs. 32 and 33 for 600° and 200° C., respectively.

By comparison with the corresponding specimens previously aged at room temperature (Fig. 31), it will be seen that neither treatment at 200° nor at 600° C. produced any effect upon the cracks in steel *D2*. In steel *D3* the number of cracks was reduced after the 200° C. treatment and to a much greater extent after the 600° C. treatment. The effect upon steels *D4* and *D5* was similar but even more marked, so that in *D5*, treated at 600° C., there were only a few dots, which might or might not be of similar origin to hair-line cracks. In all cases where the heat treatment had any effect the cracks became not only fewer but also shorter.

#### HYDROGEN TREATMENT OF LARGE SPECIMENS.

In the experiments so far reported it was necessary to quench from the soaking temperature in order to ensure the formation of hair-line cracks. This practice is subject to criticism, because it introduces severe quenching stresses, which result in a characteristic radial distribution of cracks quite different from that normally observed in industrial samples, which are usually cooled more slowly. A furnace was, therefore, specially constructed for the treatment of large specimens, and is shown diagrammatically in Fig. 17. The specimen was supported on an alundum block, *A*, which rested on a steel platform, *B*. In order to heat the specimen in a special atmosphere, a refractory tube, 5 in. in internal diameter

and closed at one end, could be lowered into position. A rubber gasket was clamped between the water-cooled steel flange fitted to the silica tube and the corresponding surface of the steel base-plate of the apparatus to give a gas-tight joint. By means of suitable vacuum taps, either hydrogen or nitrogen could be admitted to the apparatus, and the gas could be removed by a vacuum pump or passed directly into the atmosphere. A Chromel-Alumel couple

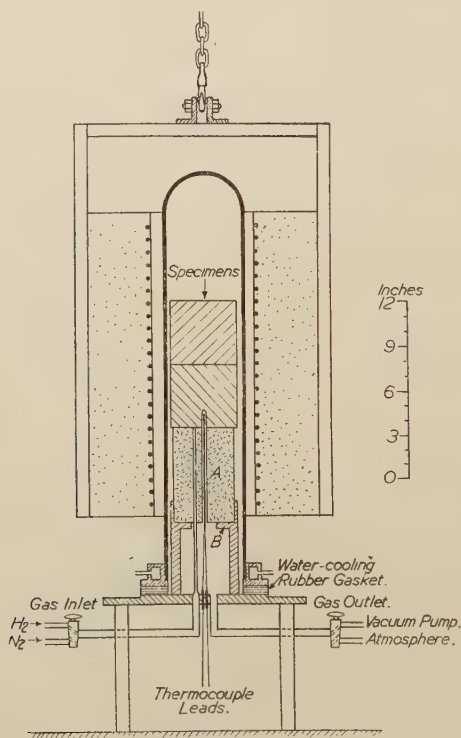


FIG. 17.—Furnace for Hydrogen Treatment of Large Specimens.

was fitted so that the temperature of the specimen could be recorded. The furnace itself was supported from a girder by means of a block and tackle, and it was possible to lift the furnace alone, or both the furnace and refractory tube simultaneously. In this way it was possible to allow the specimen to cool in the furnace, in the tube, in air, or to be quenched in water.

The steels which have so far been treated in this furnace were supplied by the English Steel Corporation, Ltd., through the courtesy of Mr. H. H. Burton, and were of the 4S11 composition in the as-cast and hot-rolled conditions. Both steels were made in the acid open-hearth furnace and the analyses supplied by



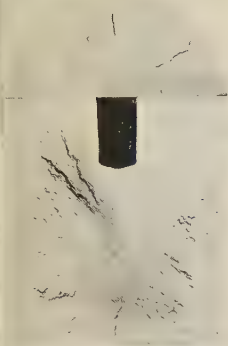


FIG. 18.—Steel 4S11, cracks revealed magnetically.

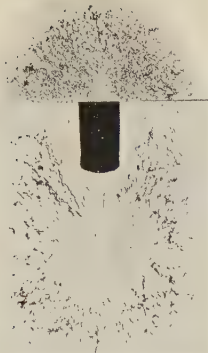


FIG. 19.—Steel 4S11, deeply etched.

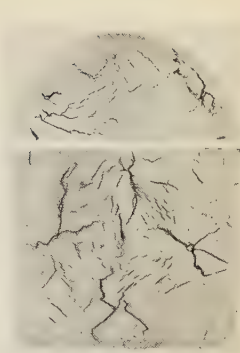


FIG. 20.—Steel F26, cracks revealed magnetically.

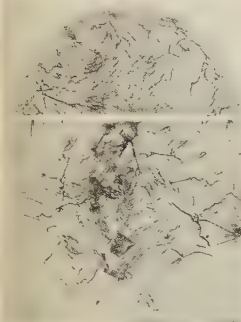


FIG. 21.—Steel F26, deeply etched.

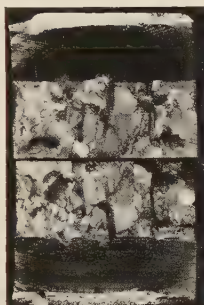


FIG. 22.—Steel F26, fracture.

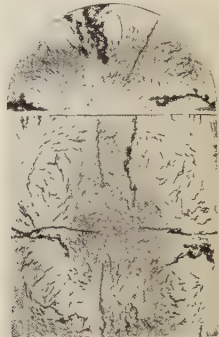


FIG. 23.—Steel F4.

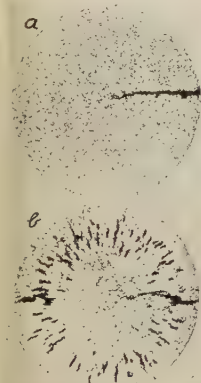


FIG. 24.—Specimen F1B, sectioned (a) 4 hr., (b) 7 hr., after quenching.



FIG. 25.—Specimen F1A, sectioned during incubation. Bottom longitudinal, top half transverse.

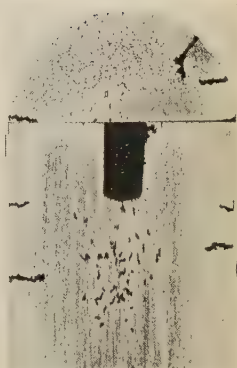


FIG. 26.—Steel 4S11, quenched in lead-tin bath at 300° C., aged at 300° C. for 1 hr.





FIG. 27.—Steel 4S11, quenched in oil-bath at  $150^{\circ}\text{C}$ ., aged at  $150^{\circ}\text{C}$ . for (a) 72 hr., (b) 1 hr.

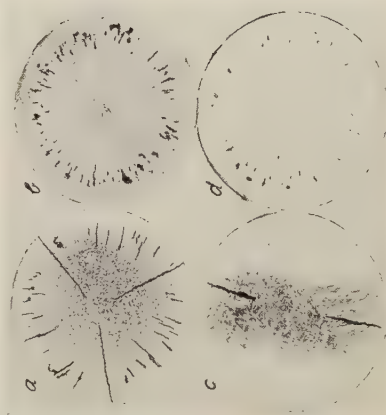


FIG. 29.—Specimen F14, aged 50 hr. at (a) room temperature, (b)  $300^{\circ}\text{C}$ ., (c)  $659^{\circ}\text{C}$ ., (d)  $475^{\circ}\text{C}$ .

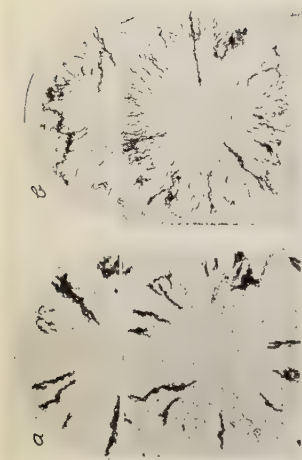


FIG. 28.—Steel 4S11, as cast, hydrogen-treated (a) as received, (b) after preliminary vacuum treatment.



FIG. 30.—Specimen F14, heated to (a)  $200^{\circ}\text{C}$ ., (b)  $300^{\circ}\text{C}$ ., (c)  $600^{\circ}\text{C}$ .

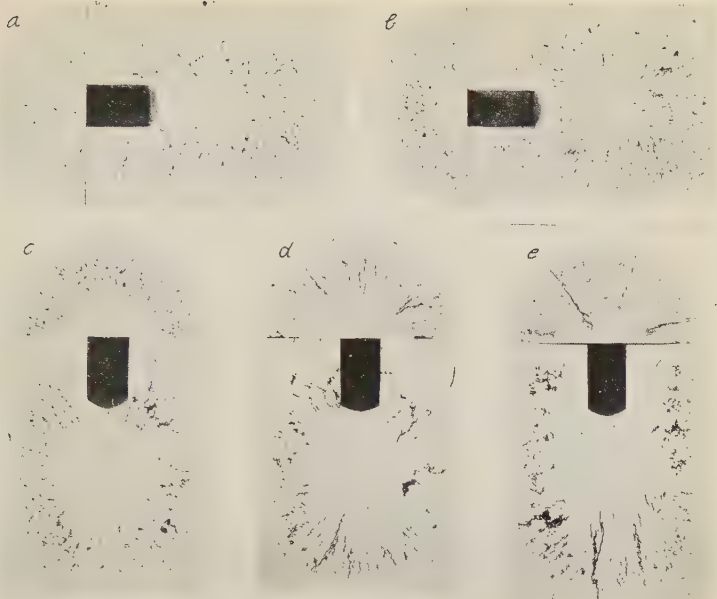


FIG. 31. —Series *D* Steel, aged at room temperature after hydrogen treatment; (a) D1 (0.08% C), (b) D2 (0.11% C), (c) D3 (0.20% C), (d) D4 (0.35% C), (e) D5 (0.44% C).

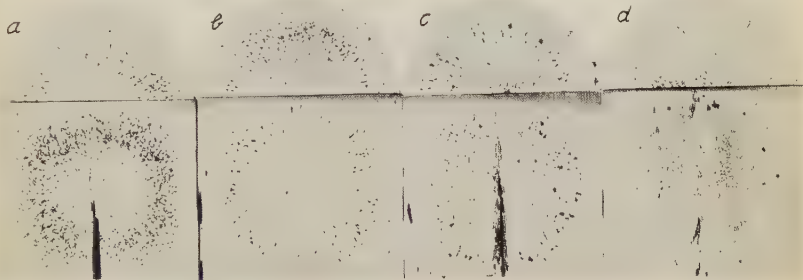


FIG. 32. —Series *D* Steel, heated to and aged at 600° C. for 24 hr. immediately after hydrogen treatment; (a) D2, (b) D3, (c) D4, (d) D5.

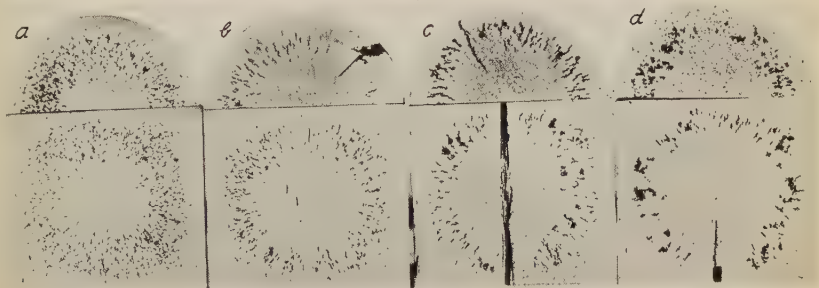


FIG. 33. —Series *D* Steel, heated to and aged at 200° C. for 24 hr. immediately after hydrogen treatment; (a) D2, (b) D3, (c) D4, (d) D5.

[Andrew & Others.

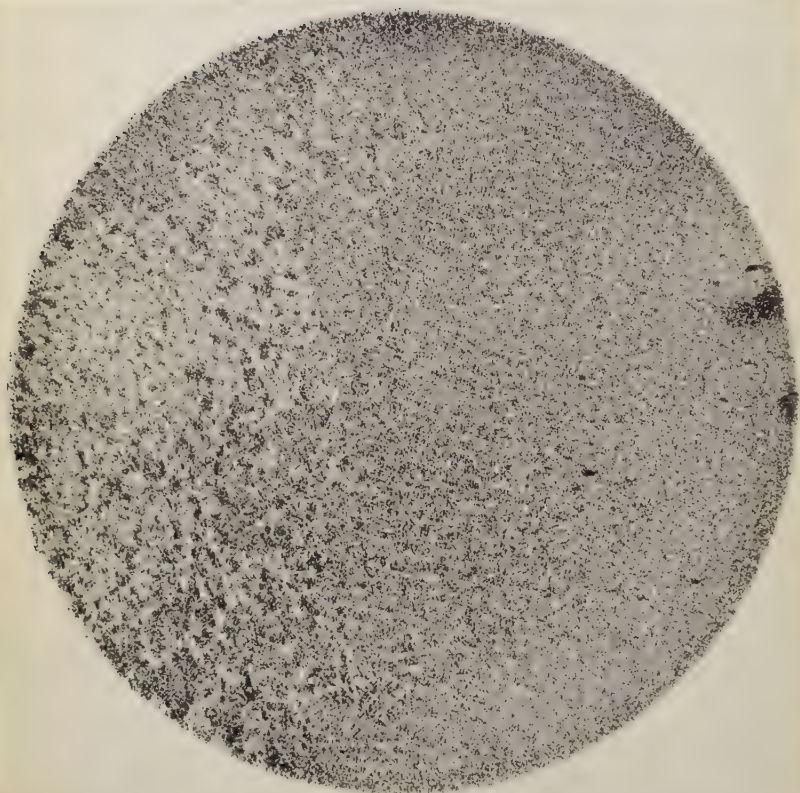


FIG. 34.—Steel 4S11, as cast, soaked in hydrogen at 1150° C. and air-cooled

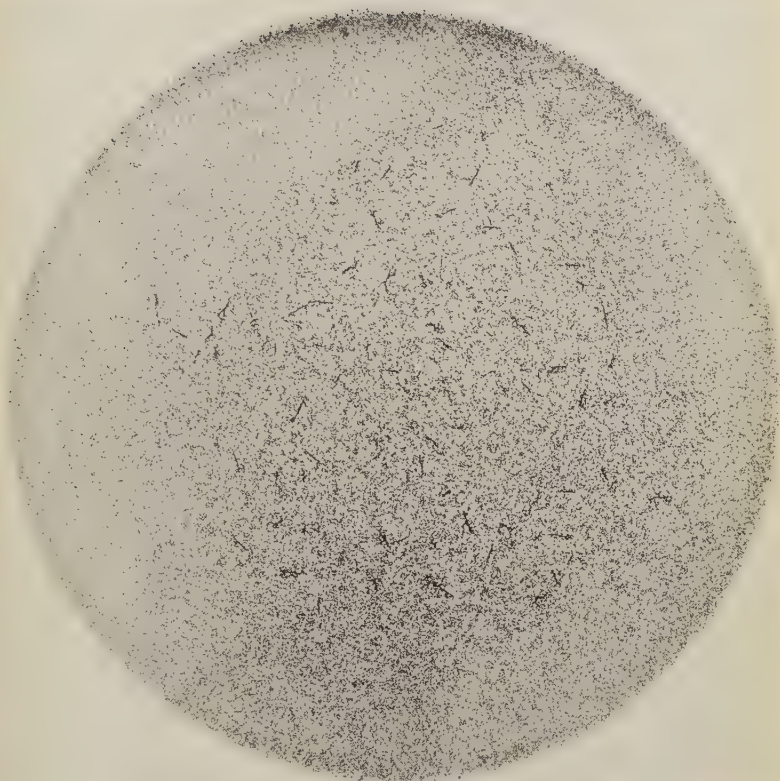


FIG. 35.—Hot-Rolled 4S11, soaked in hydrogen at 1050° C. and air-cooled.

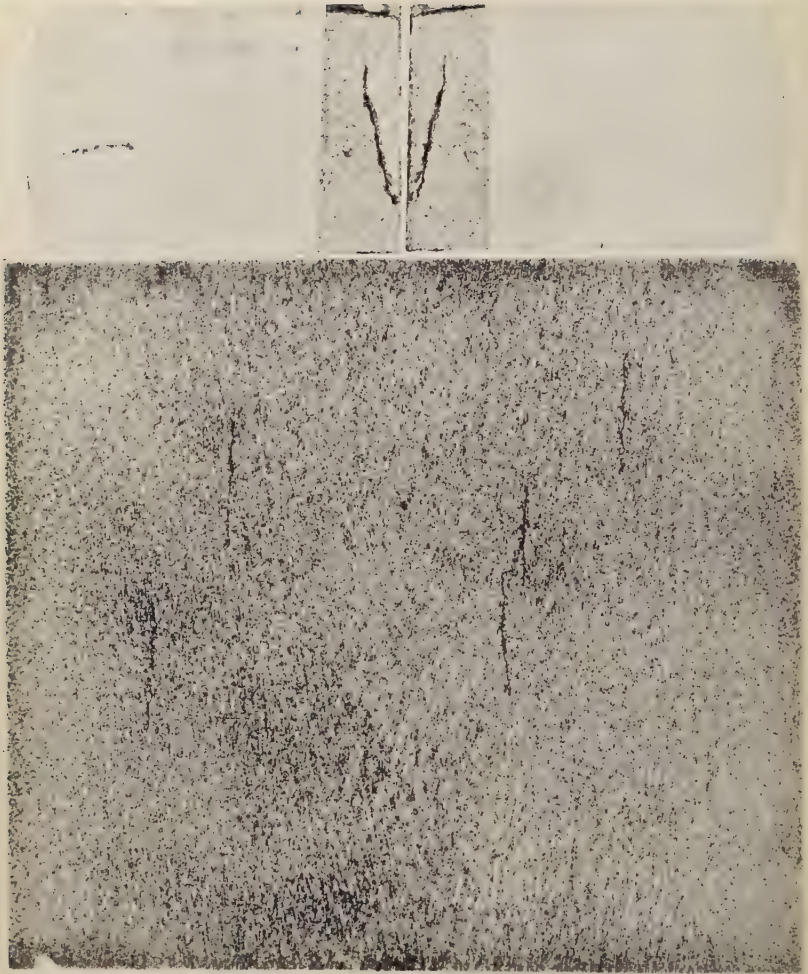


FIG. 36.—Hot-Rolled 4S11, soaked in hydrogen at 950° C. and air-cooled. *Top*, transverse fracture, *bottom*, longitudinal etched section.

[Andrew & Others.]





FIG. 37.—Steel F1, hydrogen-treated and air-cooled.  $\times 800$ .

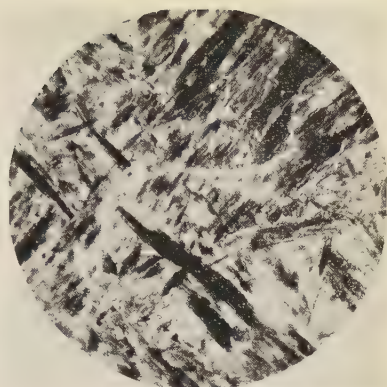


FIG. 38.—Steel F1, soaked in nitrogen at  $1200^{\circ}\text{C}$ . and water-quenched.  $\times 800$ .



FIG. 39.—Steel D1.  $\times 800$ .

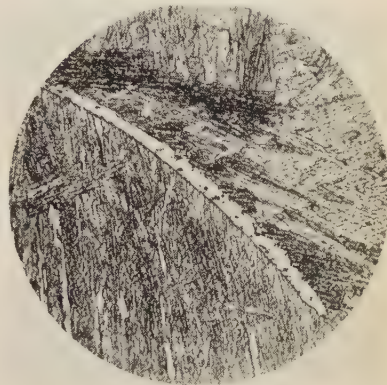


FIG. 40.—Steel D2.  $\times 800$ .

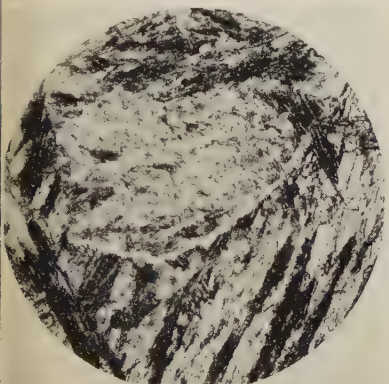


FIG. 41.—Steel D3.  $\times 800$ .

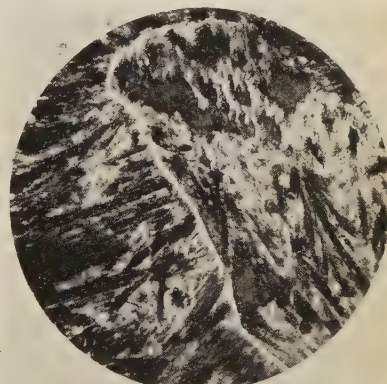


FIG. 42.—Steel D5.  $\times 800$ .

(Micrographs reduced to two-thirds linear in reproduction.)

[Andrew & Others.]

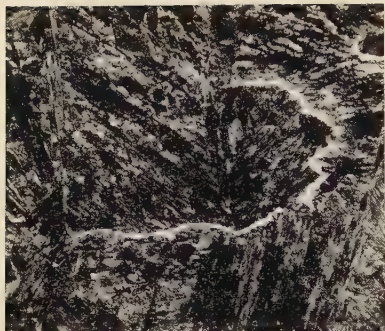


FIG. 43.—Steel F1, hydrogen-treated and water-quenched, unaged.  $\times 800$ .



FIG. 44.—Same Area as Fig. 43, aged 14 days at room temperature, repolished.  $\times 800$ .

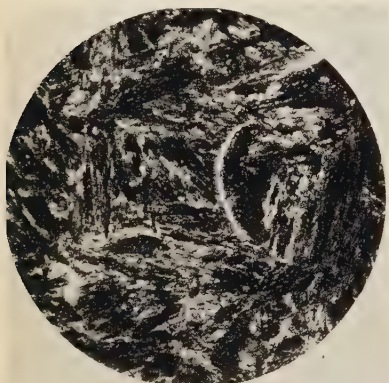


FIG. 45.—Steel F1, hydrogen-treated and water-quenched, heated to  $100^{\circ}\text{C}$ .  $\times 800$ .

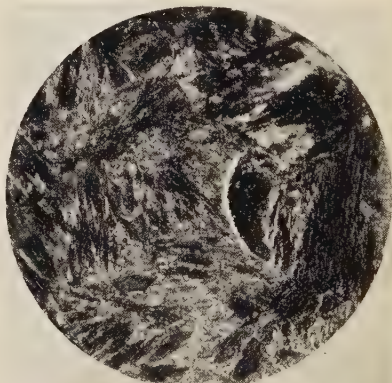


FIG. 46.—Same Area as Fig. 45, heated to  $200^{\circ}\text{C}$ .  $\times 800$ .

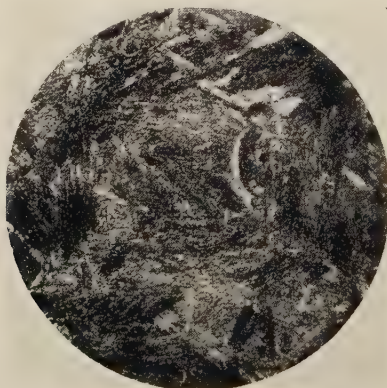


FIG. 47.—Same Area as Fig. 45, heated to  $280^{\circ}\text{C}$ .  $\times 800$ .

(Micrographs reduced to two-thirds linear in reproduction.)



Mr. Burton showed that the compositions were almost identical. The cast pieces were all machined from the lower half of a  $15\frac{1}{2}$ -in. square-sectioned ingot, the ingot being quartered for this purpose, and the round sections machined fairly close to the corner position, so that part of the circumference should be in the columnar-crystal region and part in the equi-axed region. All the specimens had been magnetically tested at the works and found to be free from hair-line cracks.

In the first experiment, two cast specimens  $4\frac{1}{2}$  in. in dia.  $\times$  4 in. long were placed one above the other on the alundum block and heated for 110 hr. in hydrogen at  $1050^{\circ}$  C. Owing to failure of the furnace winding, the specimens were then slowly cooled in the furnace in a hydrogen atmosphere. A thermal cooling curve was taken from  $550^{\circ}$  C. downwards and showed that the transformation began at  $503^{\circ}$  C. and was not complete until  $4\frac{1}{2}$  hr. later when the temperature was  $290^{\circ}$  C. The total time taken to cool from  $500^{\circ}$  to  $130^{\circ}$  C. was  $8\frac{1}{2}$  hr. The peaks on the inverse-rate curve corresponding to  $Ar_3$  and  $Ar_1$  occurred at  $459^{\circ}$  and  $367^{\circ}$  C., respectively. One specimen was sectioned 24 hr. later and the other one month after cooling. Both were examined by deep-etching and by magnetic testing, but no cracks were found. The hardness of the steel was 304 V.D.H. (Vickers diamond hardness).

In the next experiment, two cast specimens were soaked in hydrogen at  $1050^{\circ}$  C. for 150 hr. The hydrogen atmosphere was then replaced by nitrogen and both the furnace and tube were lifted so that the specimens could cool in air. The thermal curve was taken during cooling; the  $Ar_3$  peak was again pronounced at  $459^{\circ}$  C., but the  $Ar_1$  point was not apparent. One specimen was sectioned the next day and the other a month later. Little difference was observed between the two sections after deep-etching. The section of the aged specimen is shown in Fig. 34; no pronounced hair-cracks are present, but in the equi-axed region there are a few defects resembling small cracks.

Two specimens of hot-rolled 4S11,  $4\frac{1}{2}$  in. in dia. and 4 in. long were soaked for 150 hr. in hydrogen at  $1050^{\circ}$  C. and cooled in air. In addition to the  $Ar_3$  peak at  $488^{\circ}$  C., the cooling curve showed a peak at  $371^{\circ}$  C. which corresponded to the  $Ar_1$  transformation, but this change occurred over a wide range of temperature. The etched section of the specimen cut 30 hr. after cooling is shown in Fig. 35; there are numerous hair-line cracks, which are no longer in radial distribution and are deep-seated in comparison with those observed in quenched specimens. An outer rim,  $\frac{3}{4}$  in. thick, is completely free from the defect. The time taken for this specimen to cool from  $1000^{\circ}$  to  $50^{\circ}$  C. was about 4 hr., and, like the air-cooled cast specimen, the microsection showed patches of martensite. The white constituent also occurred in both cast and hot-rolled specimens, but the streaks were less prevalent and not so sharp as in the quenched steels. The hardness of the steel was 320 V.D.H.

The second specimen treated at this time was sectioned about

two months later, and the etched longitudinal section is shown in Fig. 36; there are only five very long hair-line cracks, and these are all parallel to the direction of hot-rolling. The transverse fracture shown in the upper part of the illustration includes at least two flakes, the lengths of which are comparable with those of the cracks in the longitudinal section. Although the cracks in the longitudinal section are all parallel, those in the transverse section are not. The difference in the number of cracks observed in the two specimens treated together is probably due to the fact that, with the furnace winding used in this instance, there was a pronounced temperature gradient and the temperature of the second specimen, Fig. 36, was estimated at not more than  $950^{\circ}\text{C}$ .

To confirm that the hair-line cracks observed were to be attributed to the effect of hydrogen and not to the stresses set up during air-cooling, similar, large, hot-rolled specimens of 4S11 were soaked for 150 hr. in nitrogen at  $1050^{\circ}\text{C}$ . and air-cooled. Not a single defect was observed in either aged or unaged specimens.\*

Similar experiments were carried out in which large specimens were water-quenched after soaking in hydrogen and in nitrogen. Owing to the size of the specimens, extremely severe quenching cracks were developed which almost sectioned the specimen. In the nitrogen-treated specimens, all the cracks extended to the surface. In the hydrogen-treated specimen, the cracks were more numerous and included a number of shorter ones which were confined to the interior of the metal and were almost certainly hair-line cracks.

#### MICROSTRUCTURE.

In Part I. reference was made to two different white constituents which had been observed in the microstructures examined during the course of this work. The first white constituent took the form of veins around hair-line cracks in the specimens tempered at  $300^{\circ}\text{C}$ . This constituent was undoubtedly ferrite produced by decarburisation of the steel by hydrogen stored in the cracks. The second constituent was observed in specimens examined in the as-quenched condition and generally occurred in the form of streaks at the grain boundaries.

Using small specimens, the white constituent can easily be observed in the as-quenched condition, and therefore the bulk of the work in this direction was carried out on steel F1, which could be sawn in the hardened state. Nevertheless, microsections were prepared by grinding from steels F5, 4S11, F13, F23 and F24, and the white constituent was found in all cases in the as-quenched condition after hydrogen treatment. Furthermore, the constituent

\* In view of the need for economy, a photograph of the etched section of such a specimen is omitted.

was observed in *large* specimens of both cast and hot-rolled 4S11 air-cooled after hydrogen treatment.

Illustration of the fact that the white constituent is not necessarily associated with the structure resulting from quenching is afforded by Fig. 37. In this instance, a specimen *F1A* was allowed to cool in air on a piece of asbestos board after hydrogen-soaking. Only patches of martensite were present in the specimen, whereas the white lines were almost as prominent as in quenched material. A few hair-line cracks were observed in this region, where the hardness of the steel was 375 V.D.H.

In specimens *F1A* soaked in nitrogen at 1200° C. and water-quenched, a few filaments of a white constituent were seen. At this stage it cannot be stated whether these filaments are of the same nature as those in specimens soaked in hydrogen, but, as shown in Fig. 38, they were faint and diffuse compared with the streaks associated with hydrogen (Fig. 37).

Wherever hair-line cracks were observed after soaking in hydrogen, the microsection of the steel in the quenched condition invariably contained the white constituent. Thus, the specimen of 4S11 quenched in hot oil and maintained at 150° C. for 1 hr. and subsequently aged at room temperature showed hair-cracks and the microstructure revealed quite a number of white lines. Similarly, the specimen of 4S11 soaked in ammonia at 1200° C. and water-quenched contained hair-line cracks and very prominent white filaments.

With steels of about the same carbon content a change in the other alloy content had little effect upon the appearance of the white lines. On the other hand, with steels *D1*, *D2*, *D3*, *D4* and *D5*, which were of the same alloy base but had different carbon contents, the white streaks in the outer partially decarburised rim of the low-carbon steel *D1* had the appearance shown in Fig. 39; in the interior of the specimen where the carbon content was 0.1% the white filaments were more obviously a separate constituent similar to that obtained in *D2* (Fig. 40). In *D3*, containing 0.2% of carbon, the lines had a more normal appearance (Fig. 41), whilst in *D4* and *D5*, with 0.35 and 0.44% of carbon, respectively, the white constituent stood out with increased intensity and occurred in longer streaks (Fig. 42).

In hydrogen-treated and quenched specimens, after ageing at room temperature with subsequent crack formation, the white filaments were fewer and generally less prominent than in the freshly quenched specimens. Since this observation suggested that the white constituent disappeared as the specimen lost hydrogen, quenched samples were examined at intervals. In the freshly quenched specimen, suitable areas showing prominent white streaks were marked with a diamond, and after varying intervals the section was repolished and re-etched and once more examined. The white filaments became weaker with time, some of them disappearing



completely. This type of experiment is open to criticism, since a definite amount of material must be removed each time the surface is polished and etched, and repeated polishing and etching might, in this way, remove the white constituent. This was disproved, however, by an experiment in which a characteristic area of a freshly quenched specimen, showing a fairly prominent white streak, was ringed with a diamond mark and repolished and re-etched no fewer than six times within a day; the general background was considerably changed during this process, but the white filament persisted, although its shape was modified to some extent.

A freshly quenched specimen *F1A* was sectioned and a suitable area was selected and marked with a diamond; a photograph (Fig. 43) was then taken. After a fortnight the specimen was repolished and re-etched (Fig. 44). All the characteristic background was virtually unchanged, but the white line had almost completely disappeared.

In another experiment, a suitable field in a hydrogen-treated and freshly quenched specimen of *F1* was outlined with a diamond mark and the microspecimen was then heated *in vacuo* for 15 min. at 100°, 200°, 280° and 300° C., respectively. After each heat treatment the specimen was repolished and re-etched and the microstructure examined. No appreciable change in the structure of the constituent or in the hardness of the steel was observed as the result of heating at temperatures up to 200° C. (Figs. 45 and 46). On heating to 280° C., however, the white streak became much smaller and slightly diffuse (Fig. 47), whilst the hardness of the steel dropped by 60 points to 460 V.D.H. After heating at 300° C. the white constituent was no longer visible, and at the same time the background structure was changed to that of the tempered state. Similar results were obtained when the experiment was repeated with different specimens.

A freshly quenched specimen with a marked field was dipped in a mixture of acetone and solid carbon dioxide (— 90° C.) for 15 min., but after repolishing and etching, the white constituent was unchanged.

#### GENERAL DISCUSSION OF RESULTS.

In Part I. it was shown that hydrogen was the major factor in the formation of hair-line cracks, and it was suggested that a hydrogen-rich constituent, austenitic in nature, was involved. The numerous experiments described in Part II. have afforded much supporting evidence and have enabled the hypothesis to be both strengthened and extended.

Hydrogen treatment at 1200° C. immediately followed by water-quenching was applied to many steels of various compositions, and in all cases internal cracks resulted. Similar experiments in which

the steels were soaked in nitrogen or *in vacuo* at  $1200^{\circ}$  C. before water-quenching produced no such defects. The small specimens which can be used for extensive laboratory investigations must be quenched in order to ensure cracks, and this causes a characteristic distribution of cracks which is quite unlike that met with in industrial practice. Experiments were carried out, however, on specimens sufficiently large to enable cracks to be produced by air-cooling after hydrogen treatment. The cracks so produced were characteristic hair-line cracks, deep-seated and in random distribution. Treatment of similar large specimens in nitrogen, followed by air-cooling, produced no cracks, thus proving conclusively that hydrogen is the fundamental cause of hair-line cracks.

In addition, the results obtained with large specimens justify the view that the cracks developed in smaller specimens after quenching are hair-line cracks, the quenching being necessary to retain sufficient hydrogen in the steel. The characteristic radial distribution of cracks in quenched specimens is attributed to residual stresses in the steel. The fact that residual stresses can affect the direction of cracks is borne out by those observed in industrial samples, in which the plane of the flakes is parallel to the direction of hot-rolling.

Having decided that hydrogen is the fundamental cause of hair-line crack formation, the next problem is to explain the mechanism by which hydrogen could be responsible. Of the many theories of hair-crack formation, the one which has attracted most attention is probably that due to Honda.<sup>(6)</sup> According to this theory, on a falling temperature, atomic hydrogen diffuses into voids in the steel, is there converted to molecular hydrogen and so builds up a pressure sufficient to disrupt the metal. In Part I. it was shown that immediately after crack formation the cracks were filled with hydrogen. Furthermore, if it be assumed that the width of the completely decarburised layer in Fig. 6 of Part I. is six times the width of the crack, which is a conservative estimate, and taking the equilibrium methane content at  $300^{\circ}$  C. to be 14%, the value found to apply at low pressures, then the total pressure within the cracks at  $300^{\circ}$  C. must be of the order of 50 tons per sq. in. At first sight this would appear to be excellent confirmation of Honda's theory, but in his mathematical treatment of crack formation by hydrogen pressure, Honda arrives at the conclusion that, no matter what the conditions, cracks could not be formed above  $580^{\circ}$  nor below  $200^{\circ}$  C., whereas the experiments with steels *F1* and *F5*, described above, proved conclusively that cracks are formed in quenched specimens at room temperature. Of greater importance is the fact that it is impossible to explain the sudden evolution of hydrogen associated with crack formation at room temperature in terms of Honda's pressure theory alone.

Since, in quenched specimens, a certain period must elapse at

room temperature before the cracks are developed, and since their formation is closely associated with a sudden release of hydrogen, it seems probable that the hydrogen which is directly responsible for the formation of cracks must be held in a manner which differs from pure solid solution. If it be assumed that hydrogen treatment results in the presence of a hydrogen-rich constituent in steel, it is possible to explain all the experimental results described in this paper, and in so doing to obtain further details as to the nature of this hydrogen-rich constituent. In the first place, the hydrogen-rich constituent must be regarded as metastable at all temperatures, and, for a given steel, its stability will depend upon the amount of hydrogen in solid solution in the steel. During ageing, or on heating, the amount of hydrogen in solution is progressively diminished, until a critical concentration is reached at which rapid breakdown of the hydrogen-rich constituent occurs. Some of the hydrogen thus released will diffuse into cavities or voids and there build up a disruptive pressure in the manner indicated by Honda, and the rest will escape from the specimen. The proportion of hydrogen escaping from the metal will depend upon the rate of diffusion and will account for the sudden evolution on ageing and also for the lowest evolution peak on heating unaged specimens.

With specimens of a given steel of approximately constant hydrogen content and with otherwise similar experimental conditions, the lowest evolution peak will occur at about the same temperature—for example, the 220° C. peak with 4S11. In general, however, the rapid breakdown of the hydrogen-rich constituent and the temperature at which the lowest peak on the evolution curve occurs will depend upon (i) the rate of heating, (ii) the stability of the constituent and (iii) the amount of hydrogen in solution in the steel. When the heating is slow, the hydrogen concentration will be reduced to the critical value at a lower temperature, and rapid breakdown of the constituent and the formation of cracks will occur accordingly. Similarly, rapid heating will cause the cracks to form and the evolution peak to occur at a higher temperature. This is supported by the results obtained during the heat treatment of hydrogen-treated and quenched specimens. The appearance of the cracks must be governed by the mechanical properties of the steel at the temperature of crack formation, and it was in fact found that the nature of the cracks depended upon the rate of reheating. If, in a normal low-alloy steel, the constituent decomposes at room temperature, when the steel is in a brittle state, the cracks are usually long and fine, whilst if the cracks are formed at a higher temperature at which the steel is relatively plastic, they appear wider and shorter and in the limit are virtually "dots." On the other hand, when the carbon content is low, as in steels D1 and D2, the steel will be relatively plastic even in the quenched state, and the cracks are therefore short, although formed at room temperature (Fig. 31).

It will be of interest to consider the effect of the stability of the hydrogen-rich constituent upon crack formation. It has already been assumed that the stability of the constituent is closely connected with the concentration of hydrogen in solid solution. If the constituent is unstable, little hydrogen will be lost from the specimen before rapid breakdown of the constituent occurs, and therefore there will be more hydrogen available for crack formation and the cracks will be more numerous, assuming other factors to remain constant. If the constituent is broken down by heating, instability will mean that the hydrogen is set free at a low temperature at which diffusion is slow, and from this point of view also, more hydrogen will contribute to crack formation. On the other hand, if the constituent is relatively stable, which means that it will not break down at room temperature until more hydrogen has been lost, or on heating until a higher temperature has been reached, in both cases less hydrogen will be operative in a crack formation. In the extreme case it may even be possible, with a specimen containing a stable hydrogen-rich constituent, to reheat in such a manner as to prevent hair-line cracks. Thus, it is conceivable that by sufficiently rapid heating, breakdown of the constituent might be postponed to a temperature range in which the rate of diffusion is so high that the hydrogen released by breakdown of the hydrogen-rich constituent can readily leave the metal, and no void would be able to retain hydrogen under pressures sufficient to disrupt the steel.

With the experimental conditions and the steels employed in this work, the total hydrogen retained after quenching varies only within narrow limits, and the effect of hydrogen concentration upon the stability of the constituent is not marked. On the other hand, it is clear that the composition of the steel is of major importance in determining the stability of the resulting hydrogen-rich constituent. Thus, the results obtained with the *D* series of steels can be explained only if the stability of the constituent increases with carbon content. In the first place, the temperature of the lowest peak on the evolution curve increases progressively from 50° C. for *D1* containing 0.08% of carbon to 315° C. for *D5* containing 0.44% of carbon. Additional supporting evidence is afforded by the results obtained during the heat treatment of the same series of steels. Thus, with the steel of lowest carbon content, *D2*, heat treatment produced no effect upon the number of cracks, because the constituent was very unstable, and in all cases cracks were formed at or near room temperature. With increasing carbon content, *D3*, *D4* and *D5*, the effect of heat treatment upon hydrogen-treated and quenched specimens was more and more marked. As already described, steel *D5*, treated at 600° C., showed only a few dots, which is in keeping with the fact that this steel had the highest carbon content, so that the constituent was more stable and, with this rate of heating, did not decompose until a relatively high temperature was reached.



In general, the gas evolution at room temperature fitted in with the ideas of stability put forward above. When the incubation period was short—that is, the constituent was relatively unstable—the total amounts of hydrogen evolved were larger and more numerous cracks were observed. With the *D* steels the evolution of gas at room temperature fell with increasing carbon content, and this is probably to be attributed to two separate effects: First, the greater stability of the constituent and, secondly, the larger amounts of methane formed in steels of higher carbon content. The methane content of gas samples collected from the specimens was usually low, and can bear no direct relationship to the methane contained in the cracks, since methane, as such, cannot diffuse through the metal. The methane actually analysed was usually formed by reaction between evolved hydrogen and the carbon contained in the surface layers of the specimen, and this accounts for the remarkable constant methane percentages observed in the experiments with steel 4S11. On the other hand, when the nitrogen content of the steel was high, as in the case of ammonia-soaked forged 4S11 and hydrogen-treated cast 4S11, some of the cracks extended to the surface. In cases like these the percentage of methane in the gas sample was high, even when the gas was evolved at room temperature, and this must be taken as evidence that the cracks contained considerable quantities of methane. Owing to the fact that hydrogen will diffuse to the surface of the cracks in the atomic state and will therefore be intensely active, and because of the high pressures which must exist within the cracks, the formation of methane, even at room temperature, is not surprising. The top peak on the evolution curve obtained on heating has already been attributed to the breakdown of methane, but it is not possible, in the case of aged specimens, to say whether all this methane already existed in the cracks at room temperature or whether it was formed during heating. In the specimens heated for evolution immediately after quenching, the methane, like the cracks, must have been formed during heating. As might be expected with the *D* steels, there was a general tendency for the magnitude of the methane peak to increase with the carbon content of the steel.

During the investigation of the effect of the soaking time in hydrogen upon crack formation in steel 4S11, it was found that, although there was only a small difference in the total hydrogen content from the shortest to the longest time of soaking, nevertheless, the number of cracks differed considerably. This suggested that the shorter the time of soaking, the less effective was the hydrogen in crack formation, a conclusion which is borne out to some extent by the results obtained on the tantalum steel. In this case the longer the period of soaking the less was the hydrogen evolved at room temperature per unit length of crack formed in the longitudinal section of a standard specimen.

It has been suggested that, with a given steel and a given



hydrogen treatment, the hydrogen concentration must be reduced to a critical value before the rapid breakdown of the hydrogen-rich constituent can occur. While this suggestion is necessary in order to explain the results obtained, it is difficult to give direct experimental confirmation. Nevertheless, with the plain carbon steel *F26* the same amount of hydrogen was evolved before the sudden evolution associated with crack formation, whether the specimen was aged at room temperature or was heated to 150° C. immediately after quenching.

It will be realised that many of the properties postulated above for the hydrogen-rich constituent are those actually observed for the white streaks which were such a prominent feature of the microstructure of hydrogen-treated and quenched steels. The white streaks disappear with time, both at room temperature and on heating, and the intensity and sharpness of the streaks increase with the carbon content of the steel. In Part I. it was stated that the microconstituent was austenitic in nature, and no result contradictory to this view has yet been obtained. Granted the austenitic nature of the white streaks and linking them with the hydrogen-rich constituent postulated above, it becomes possible to account for some of the effects of alloying elements upon hair-line crack formation. Thus, carbon or carbide-forming elements such as chromium or manganese would be expected to stabilise the constituent, whilst graphitising elements, such as nickel and silicon, should render it unstable.

It is not intended to suggest that each white streak observed in the microstructure would normally develop into a hair-line crack. The microconstituent probably serves only as a storage place from which hydrogen may subsequently be released, to form cracks by building up high pressures in voids. The positions of the cracks developed will be governed by the voids and other weaknesses existing in the steel, and stresses may play an important part.

As already shown, when the hydrogen-soaked specimen 4S11C was air-cooled, it lost very little hydrogen in the  $\gamma$  region, and this is probably due to the low rate of diffusion of hydrogen in  $\gamma$ -iron. On the other hand, the drop in hydrogen solubility at the  $\gamma$ - $\alpha$  change must have an important bearing on the formation of the constituent. All the results so far obtained suggest that, given an initially high hydrogen content in the steel, the hydrogen-rich constituent is formed whenever the specimen is cooled too rapidly through the  $\gamma$ - $\alpha$  change for the solubility/temperature curve to be followed. The critical rate of cooling will be governed by various factors, the most important being the size of specimen and the temperature of the change point. The larger the specimen, the greater is the distance through which hydrogen must diffuse, and therefore the slower is the rate of cooling necessary to avoid the retention of hydrogen. The higher the change point, the greater

is the rate of diffusion and therefore the less is the time required for the surplus hydrogen to diffuse out of the steel.

With the specimens employed in this work, crack formation at room temperature was accompanied by the evolution of much of the hydrogen originally contained in the steel, and was followed by further gradual evolution. It might be supposed, therefore, that a method of avoiding hair-line cracks in the finished product in industry would be to expel the hydrogen by allowing hair-line cracks to develop, ageing and reforging. In many cases such a treatment would probably be successful, but there is the danger, particularly with steels of high carbon content, that the methane stored in the cracks and unable to escape at low temperatures would, on reforging, break down and release sufficient hydrogen to saturate the steel once more and so give rise to a new series of cracks on cooling.

Bearing the methane in mind, it is clear that any attempt to expel hydrogen by heat treatment must be carried out at as high a temperature as is possible within the  $\alpha$  range. Whilst a low-temperature treatment may be satisfactory for the removal of hydrogen as such, it would fail to overcome the trouble arising from methane.

#### CONCLUSIONS.

The work described above has led to the following conclusions :

- (i) Hydrogen is the fundamental cause of hair-line cracks.
- (ii) The hydrogen which subsequently causes cracks is not in solid solution, but, for a time, is held in the form of a hydrogen-rich constituent which is formed on rapid cooling through the  $\gamma$ - $\alpha$  change.
- (iii) Breakdown of the constituent releases hydrogen, some of which diffuses into voids and builds up a disruptive pressure.
- (iv) In addition to hydrogen, the cracks contain methane, even at room temperature, and the presence of this methane is the cause of some of the difficulties encountered in the industrial prevention of hair-line cracks.
- (v) The influence of composition upon the susceptibility of a given steel to hair-line crack formation is explained by the effect of alloying elements upon the stability of the resulting hydrogen-rich constituent.
- (vi) Once the constituent has been formed, its breakdown at low temperatures must lead to hair-crack formation. On the other hand, hair-line cracks will not result if breakdown of the constituent can be brought about at a sufficiently high temperature.

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[This paper was discussed jointly with the two preceding ones by Professor J. H. Andrew, H. Lee and A. G. Quarrell on "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys" and by Professor J. H. Andrew, A. K. Bose, G. A. Geach and H. Lee on "The Formation of Hair-Line Cracks.—Part II."]

*JOINT DISCUSSION.*

At a Joint Meeting of the Sheffield Society of Engineers and Metallurgists, the Sheffield Metallurgical Association and The Iron and Steel Institute, held under the Chairmanship of Dr. W. H. Hatfield, F.R.S. (Vice-President of The Iron and Steel Institute; President of the Sheffield Society of Engineers and Metallurgists) at the Royal Victoria Station Hotel, Sheffield, on Saturday, 24th October, 1942, three papers on "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys," by Professor J. H. Andrew, H. Lee and A. G. Quarrell, "The Formation of Hair-Line Cracks.—Part I.," by Professor J. H. Andrew, A. K. Bose, G. A. Geach and H. Lee, and "The Formation of Hair-Line Cracks.—Part II.," by Professor J. H. Andrew, A. K. Bose, H. Lee and A. G. Quarrell, were presented and discussed jointly.

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Dr. H. LEE presented the paper on "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys" and Dr. A. G. QUARRELL the two papers on "The Formation of Hair-Line Cracks."

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S., Brown-Firth Research Laboratories, Sheffield) : We are indebted to Dr. Lee and Dr. Quarrell for introducing the papers for discussion. Our academic friends seem to be obsessed with the influence of hydrogen in this matter—far more than I am, at any rate—and I will take part in the discussion later on. In view of the very considerable work that he has done in this field I will ask Mr. Burton to open the discussion.

Mr. H. H. BURTON (English Steel Corporation, Ltd., Sheffield) : The portions of these papers which I find particularly interesting are those dealing with the positions on the heating and cooling curves where hydrogen is evolved most easily. As I, naturally, have not taken part in this actual work, I do not feel in a position to criticise the question of the theory based upon the hydrogen-rich complex, but I would like my part in the discussion to take the form of suggesting one line on which such experiments might be conducted, and which, I think, if followed, might give us some information which would be of real practical value in the works. The curves, as I understand it, that have been published showing the evolution of hydrogen after reheating were all obtained from specimens which had been cooled completely to atmospheric temperature. It seems to me very important that these experiments should be repeated on specimens which have been saturated with hydrogen and only cooled down to a temperature of about 300° C. before being reheated to, say, 650° C., which would bring the experiment in line with the type of precautionary treatment which we in the works find most valuable. The second suggestion I would make is that, using a steel such as a 3%, or 1½%, chromium-molybdenum steel, which could be transformed readily in the



pearlitic range, the experiment should be repeated of saturating such specimens in hydrogen, cooling them down through the range of temperature where transformation will occur at the pearlitic range, then both quenching some specimens rapidly thereafter and also cooling others down slowly and reheating them, to see where and how the hydrogen is evolved. I think that would be a most important extension of the work already done.

I do not know whether any of us in Britain have had the experience of hair-line cracks being formed when the steel is, shall we say, in a more or less stress-free condition after passing through the transformation. Houdremont seems to suggest that in some cases, by saturating even after passing through the change, and cooling down again, when there is presumably little or no thermal stress present, he can obtain hair-line cracks. That, I think, is another very important matter to be decided, and it seems to me that it might be decided most effectively by experiment with steels which could be transformed in the pearlitic range.

I personally have been extremely interested in the work done by Professor Andrew and his colleagues, and I feel that we are really getting to the point when we may be able to understand hair-line crack formation very much better than in the past.

Mr. D. A. OLIVER (Messrs. Wm. Jessop & Sons, Ltd., Sheffield) : This work on hair-line cracks has developed from the repetition of the early Musatti and Reggiori experiments, and the authors have devised additional experiments which have led to a real advance in the knowledge of the subject. The primary discovery, in my judgment, is the spontaneous evolution of gas, largely hydrogen, after a period called the incubation period. Another important feature which they have discovered is that if the specimen is cooled right down to room temperature, then reheating at that stage but prior to actual cracking does not subsequently prevent the specimen from cracking ultimately; that in my opinion is a significant fact from the point of view of planning to avoid trouble in large masses of steel during manufacture.

On the side of the theory, I think it must be said that the explanation put forward is not entirely conclusive, but it is one which I consider should be sympathetically examined. I find myself in a less advanced stage to that of the authors in drawing final conclusions, because of such questions as these: Are all the cracks associated with special constituents, or are some of the cracks of this character and are the remaining ones just stress-relieving cracks in the neighbourhood? This question is important, because it may be necessary to hunt for the primary cracks while regarding others in the vicinity as purely incidental. A further question arises as to whether there are any alternative ways of explaining the experiments without resorting to the postulation of a new constituent involving unusual properties. Surely the sup-



position of patches of austenite retained on cooling with the interstices filled with hydrogen atoms under pressure goes a long way towards a means of explaining the experimental facts. Furthermore, we should keep our minds open to an even more subtle interpretation of the whole subject. I believe that Professor Fowler's work<sup>1</sup> has indicated that hydrogen might go into solid solution in a metal and even break down to a lower state than the atomic one—that is to say, we might ultimately have to consider hydrogen atoms, protons, and free electrons; and it is interesting that nickel, which is an element hungry for electrons, is also an element which, when added to carbon steel, increases its susceptibility to hair-line cracks. If we imagine the electrons in some of the hydrogen atoms to be firmly attached to the nickel atoms, then we might have to visualise in the structure free protons of which the recombination to hydrogen atoms would depend upon the separate supply of electrons. I am throwing this out only suggestively, as there may be ultimately a far more involved explanation of the matter than that of merely a new phase transformation.

Another matter of interest is the conception of voids, which the authors, perhaps wisely, have not precisely defined. We are gradually getting more information on the nature of cracks that occur in polycrystals, and we may picture, at the junction of two crystals, a number of randomly arranged fragments of perfect crystals having small misfits at the junction. I think that from one angle those might serve as quite useful initial voids, but on the other hand they may not be large enough, and what is rather mystifying is that hair-line cracks appear to occur not only along boundaries but also in transcrystalline directions as well. I think it would be helpful if in future work we could have from the authors a fuller statement of their conceptions of the voids which they imagine necessary to constitute pockets into which atomic hydrogen can diffuse, thus to form molecular hydrogen and so to build up high pressures.

The reference to the rôle that methane plays is of particular interest, in that the first detailed suggestion has been put forward as to how it may play an important part in practice.

Dr. R. J. SARJANT (Messrs. Hadfields, Ltd., Sheffield): It is essential to distinguish between the conditions used in the experiments reported and those obtaining in actual practice, both as regards size of material considered and the gas content to be found in the two cases.

In the experiments described, slow cooling through the  $A_1$  point could be followed by quick cooling and sound material resulted. It is questioned whether the same would apply with larger masses. Houdremont's work, confirmed by many other

<sup>1</sup> R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," p. 560. Cambridge, 1939.

experiments, indicated that there are much lower limits determined by both the mass and the susceptibility of the steel, to which slow cooling must be continued in order to ensure soundness, provided that no other special remedial treatment has previously been applied.

To those who believe that hydrogen plays a part in the formation of hair-line cracks a clearer picture is obtainable from the experiments of Professor Andrew and his colleagues of the mechanism of the changes in the steel giving rise to the formation of flakes. The authors postulate the formation of chemical compounds. The existence of compounds, possibly hydrides of chromium, manganese and nickel, was suggested by Esser, Eilender and Bungeroth,<sup>1</sup> and these may be regarded as being capable of breakdown with the formation of internal pressure from the hydrogen liberated. Greater diffusion of the gas could be regarded as taking place at the higher temperatures, and building up of pressure at the lower. Bennek and Klotzbach<sup>2</sup> showed that there was a greater solubility of hydrogen in the  $\gamma$  condition and a greater diffusibility in the  $\alpha$ . On cooling down to the change point hydrogen was liberated, and, provided that the change took place at a high enough temperature, could diffuse away, given sufficient time. In the  $\alpha$  condition there is less internal space, and therefore conditions after passing the change point are likely to produce a building-up of hydrogen pressure. Zapffe and Sims<sup>3</sup> referred to rifts in the mosaic structure of the metal, and the more ready occurrence of flaws in forged material than in cast indicates that the space factor in the building-up of pressure is significant. In fact, the rift-mosaic theory of these workers explained other defects associated with the action of hydrogen. Thus, the most interesting facts revealed in this work are to be looked for in the character of the hydrogen evolution curves.

As to whether a chemical compound is produced and whether the pressure is built up in voids there is as yet insufficient evidence to allow one to become dogmatic, but the facts can all be explained on a physical basis, when the general adsorption characteristics of gases on surfaces are taken into consideration. Such adsorbed gas within the structure of the steel could be expected to influence markedly the physical characters of the material, particularly under conditions of stress, and could account for the phenomena without the need for postulating a theory involving the building up of internal pressure, which appeals to me as untenable.

Of those who oppose the view that hydrogen must be entirely excluded from the explanation of the cause of hair-line cracks the question is asked "Why do the types of steel vary so widely in

<sup>1</sup> *Archiv für das Eisenhüttenwesen*, 1935, vol. 8, Mar., pp. 419-423.

<sup>2</sup> *Stahl und Eisen*, 1941, vol. 61, June 19, pp. 597-606; June 26, pp. 624-630.

<sup>3</sup> *American Institute of Mining and Metallurgical Engineers*, 1941, *Technical Publication No. 1307: Metals Technology*, Aug., 1941.

susceptibility from one process to another, from one furnace to another and even from one cast to another ? ”

In order to throw further light on the subject it is suggested as an extension of the present work that the dilatometric changes in the steel throughout the heating and cooling cycles should be explored in conjunction with the character of the gas evolution and the susceptibility to produce flaws.

Dr. E. GREGORY (Hon. Member of Council of The Iron and Steel Institute ; President of the Sheffield Metallurgical Association ; the Park Gate Iron and Steel Co., Ltd., Rotherham) : With regard to the first paper, on the determination of the solubility of hydrogen, there is just one point in connection with Fig. 5 which to my mind is important and which apparently Dr. Lee did not stress, namely, the very important conclusion, if it is true—and one is quite prepared to accept it—that nickel apparently very considerably increases the solubility of hydrogen in both  $\alpha$ - and  $\gamma$ -iron. That, I contend, is a very important conclusion.

Regarding Part I. of the paper on the formation of hair-line cracks it is stated in the summary that “hydrogen must be regarded as the major factor operative in hair-line crack formation.” Personally, I do not agree. I think that the major factor in the development of hair-line cracks is the volume change accompanying the  $\alpha$ - $\gamma$  transformation in the steel, although, of course, the difference in the solubility of hydrogen in  $\gamma$ - and  $\alpha$ -iron may be a contributory factor. I would ask the authors whether they consider that, if iron exhibited no allotropy, hydrogen would indeed bring about crack formation ?

In Part I., the authors record the results of some experiments on conical sections. These are indicated in Fig. 1, and at the bottom of p. 195 P they state that “no cracks were observed in those parts of the specimen which were less than 2 cm. in dia.” I should like to ask why ? Was it a question of the rate of cooling and the retention of austenite, and, therefore, the difference in the solubility of hydrogen in  $\gamma$ - and  $\alpha$ -iron ?

Both Mr. Oliver and Dr. Sarjant have referred to the question of voids, and personally I should appreciate some further explanation in regard to the nature of these voids, into which the hydrogen is supposed to diffuse.

In regard to Part II. I have only one comment to make. The authors develop these hair-line cracks by pickling in strong hydrochloric acid, but I venture to suggest that pickling in acid may develop cracks which were non-existent in specimens subjected to the magnetic crack detection method. Under such circumstances, the cracks may be purely the result of stress-relief. Any hardened steel, we know, must be internally stressed to a very high degree, otherwise it is difficult to account for the enhanced hardness of quenched steel, and it has been stated that the best way to crack any

hardened steel is to pickle it. From my experience the "Magnaflux" method will often reveal minute cracks which are not revealed by hot-etching.

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S.): I personally should not like my expression that these papers were of an academic nature to be wrongly construed. As a matter of fact, I meant what I said for this reason, that these experiments have been done under conditions far removed from the conditions of works practice where the phenomenon of hair-line cracks is encountered; that is, the authors have conducted these experiments in the presence of an excessive amount of hydrogen. Time, temperature and hydrogen have been employed to exaggerate any effect which hydrogen might have, and in that sense, I think, you will all agree that these experiments must be regarded as of an academic character.

Now let us think of what the real facts are; there are a few which we cannot avoid conceding. The first fact, of course, is that it is not all our steel that suffers from hair-line cracks; it is only a very small proportion of it, even when not specifically treated to prevent hair-line cracks. The second point is, what is the actual amount of hydrogen present in commercial steels? Well, that is very simple: It is of the order of 0.0001%. Very little hydrogen indeed is found in commercial steels. We have of late established that when steel is liquid it does normally contain considerably more hydrogen in solution. One of my colleagues, Dr. Newell, has found that molten steel can contain many times as much hydrogen as is found in the solid steel, and it is established that hydrogen is gradually lost as the steel cools from the superheat temperature to the solidifying range, that when the steel solidifies there is very little hydrogen remaining, and that what little there is progressively departs in the subsequent course of hot-working operations.

Now, those are the facts, so that what we are considering is the appearance of this phenomenon of hair-line cracks in the relative absence of hydrogen, as compared with the conditions provided by the authors in their experiments, and the reasons that I have now given are the reasons why it has not been necessary for a moment to contemplate in any serious way the part played by hydrogen in forming hair-line cracks.

I have for a long time held, and discussed in Committee, that the transformation in itself is so serious in its effects and its possibilities that there was no need to look much further afield for the cause of hair-line cracks. You see, if you take a large mass of nickel-chromium steel—2 or 3 tons—put a thermocouple in it and cool it relatively quickly, you will actually get the evolution of heat at the transformation at a temperature of from 400° to 300° C. It is quite clear that when that transformation takes place you have volume changes which in themselves are very serious, and you have to consider that that transformation does not pass through the material



quickly; it commences at different nuclei, just as when you look through a microscope and see the troostitic formation in spots. It is an analogous principle to that which applies in the transformation change as it takes place in a mass of steel. Imagine a transformation taking place—as indeed it does—actually at a temperature of  $400-300^{\circ}$  C., when the steel has already become relatively incapable of ready plastic deformation, and consider the immense stresses which would be set up. Now, on the other hand, if you cool that same mass of nickel-chromium steel, weighing tons, very slowly, as I have done, that transformation will take place at  $650^{\circ}$  C.; in other words, the volume changes will be brought about at a temperature at which the steel is extremely plastic.

There is also another important fact. It is frequently said that if, in the initial ups and downs of treatment, you are careful to handle the steel properly, you may subsequently operate during these changes without causing damage. I think that is to be explained by the consolidation of the structure through hot-work and through the recrystallisation which has taken place in the time-temperature manipulation. Now, if this suggestion which I am explaining to you is true, it would follow that in a plain carbon steel, in which you do not depress the transformation and in which the transformation always takes place at a temperature at any rate approximately similar to that of equilibrium conditions, you would not expect to find hair-line cracks. Bearing on this, it may interest you to know that carbon steel does not suffer from hair-line cracks, and there, I consider, we have a demonstration of the utter importance of the transformation change; the inclusion of hydrogen in a contemplation of this interesting subject is unnecessary.

I agree that the subject is very complex. Even the data which we have as a Committee collected during the last few years are yet insufficient and unagreed. I have this morning received from Mr. W. J. Dawson, of Hadfields, a summary of his Company's experiences concerning the order in which different steels should be placed as regards their liability to suffer from hair-line cracks; the order is very interesting, and is as follows (the highest susceptibility comes first): Manganese-molybdenum steel, chromium-molybdenum, chromium, nickel-chromium-molybdenum, nickel-chromium, nickel, nickel-molybdenum steel; and, of course, it omits the carbon steels, because the matter does not arise. Our order is entirely dissimilar to Mr. Dawson's; for instance, next to the most susceptible steel is the nickel-molybdenum; we find the nickel steels very susceptible, particularly if they have very low carbon contents; the manganese-molybdenum steel is quite low down the scale. So that, you see, until we can become more fully agreed as to the details of the phenomenon and of the circumstances under which it occurs, one cannot be arbitrary, and therefore I am not pretending to be arbitrary to-day. I merely desire to contribute a little to the discussion.



I would like to point out, on behalf of both Mr. Dawson and ourselves, that these steels of which we give the order of susceptibility are steels the whole of which we produce without producing hair-line cracks. The order of susceptibility is the result of experiments made to see how these different steels behave when the conditions which we know must be fulfilled to prevent hair-line cracks are not fulfilled. It is pretty obvious that if the transformation leading to volume change can occur in certain steels at temperatures so low that the steel is not sufficiently plastic to yield without rupture, then you will have hair-line cracks. If you provide treatment which ensures that the transformation does take place at temperatures where the steel is plastic and where damage cannot be done, you will not have hair-line cracks. I do suggest, therefore, that I have explained hair-line cracks without resorting to this idea of hydrogen.

Mr. T. F. RUSSELL (English Steel Corporation, Ltd., Sheffield) : Everyone who has followed closely the work being done by Professor Andrew and his co-workers at Sheffield University on the effect on steels of soaking them in hydrogen at very high temperatures and for long times cannot fail to be impressed by the tenacity with which the investigators are clinging to the hydrogen theory of hair-line cracks. I share in the general admiration of the high quality of the work which they are doing, but what I admire most of all is the mental agility displayed by the authors in interpreting nearly every experimental result as evidence in favour of their theories.

The authors are very emphatic in their statement that hydrogen is the *fundamental cause* of hair-line cracks, but I would remind them that when looking for a fundamental cause of anything one usually has to go very deeply into the problem. As far as hair-line cracks are concerned, one could start a search for their cause by acknowledging a few indisputable facts, of which I mention three :

(1) It is an essential condition that a body must be in a state of stress before rupture can take place.

(2) The place where a crack starts is that place where, at the time of crack formation, the tensional stress exceeds the resistance to stress of the material at that place; in other words, where the ratio of the stress present to the resistance of the material in that locality is not less than unity.

(3) It follows directly from the last statement that, if a crack forms, that crack is not necessarily either at the place where the stress is a maximum or at the place where the material is weakest.

Unfortunately, one cannot go much further without entering into the realms of controversy, but sufficient has already been said to make it understandable why different observers have at different times associated hair-line cracks with non-metallic inclusions,

ghosts, dissolved gases, dendritic structures, crystal boundaries, martensite and indeed almost every imaginable thing that causes a discontinuity of physical properties. The authors now seriously ask us to believe that hydrogen is the *fundamental cause* of hair-cracks. That is tantamount to saying that in the absence of hydrogen no internal stresses sufficiently high to cause hair-line cracks could be set up in steel. I do not accept this view; I believe that every separate hair-line crack—or any crack—is caused by a circumstance or set of circumstances which enables the second of the above-mentioned conditions for crack formation to be satisfied. In the same piece of hair-line-cracked steel these circumstances may vary from crack to crack. Every factor which tends to increase a local stress, or, alternately, tends to lower the local resistance of the steel, in such a way that the former exceeds the latter, must be put amongst the “contributory causes” of hair-line cracks. Although hydrogen must be placed in this category, I do not know of an experimental result or theoretical dissertation which throws any light on the relative potency of hydrogen as a hair-line crack former when it is present in such quantities as are found in commercial steels.

The authors seem to lay special emphasis on the experimentally proved fact that quenching a steel which has had a prolonged soaking at a high temperature in a vacuum or in nitrogen does not produce any cracks, whereas when hydrogen is used cracks are formed. I am not at all impressed by this result. At high temperatures nitrogen is a comparatively inert gas but hydrogen is a very reactive one. By the authors' own showing, hot hydrogen will reduce oxides, lower the carbon content and, I think they might have added, lower the sulphur content. The reduction of oxides, even if they were sub-microscopically small, would create “voids.” Some of these voids might conceivably be the seats of hair-line cracks for three reasons: (a) They would weaken the resistance of the material in their vicinity, (b) they would cause a local concentration of the body stress, and (c) they would be suitable places into which the hydrogen could diffuse, and this may still further increase the stresses already present. This latter effect, *i.e.*, the diffusion of hydrogen into the voids, is one which requires time and is one of the possible explanations of the “period of induction” before cracks are formed. Whether the creation of voids by the hydrogen treatment is the correct explanation of the authors' main result or not, there is no doubt whatever that to soak any steel in hydrogen at 1250° C. and then to quench it in water is a drastically punishing treatment. No wonder that its “body” may be so weakened and its “personality” so subdued that it cannot face up to the stresses finally imposed upon it!

In works practice we do not give steel any treatment which even resembles this, and I think we shall have to look more carefully into the potentialities of other factors which can set up the local stresses essential for hair-crack formation.

If steel were perfectly homogeneous we would be concerned only with body stresses, of which the two causes are temperature gradients and phase changes. Of these the latter is by far the more important, particularly if the phase change takes place at temperatures below about 500° C., when the steel has lost much of the plasticity that it had at higher temperatures. Even in the ideal case of homogeneous steel the determination of the body stresses would be extremely complicated, as not only do they change during the time of cooling, but they are influenced by the relaxation and redistribution of stress due to plastic deformation. Fortunately for the steel-treater, the two systems of body stresses caused by temperature gradients and phase changes, respectively, tend to neutralise one another, and general experience has shown how to keep the resultant body stresses under such control that if they were the only stresses present there would be no more trouble with hair-line cracks.

Commercial steel, however, is not homogeneous, and its heterogeneity gives rise to other systems of stresses brought about by the juxtaposition of constituents having different physical properties, concentration gradients in the primary crystal, the presence of non-metallics, &c. These stresses have frequently been referred to as micro-stresses. This is not a very satisfactory name, as it may give the impression that the stresses themselves are very small. Actually, they can be very large, although they act over a relatively small area or through a small volume.

These stresses have been the subject of a very careful study by Laszlo, who has aptly named them "tessellated" stresses.<sup>1</sup> On the question of hair-cracks his conclusion is that hydrogen pressure and the stored energy of tessellated stresses due to cooling are the causes of hair-cracks, but, personally, I think that these tessellated stresses, particularly when superimposed on body stresses, which are by no means negligible when large masses are concerned, may be sufficiently large to cause hair-cracks. If hydrogen is present in sufficient quantities it may help to increase the stress up to the requisite amount to cause hair-cracks, but I have still to find any evidence that hydrogen is either the fundamental cause or even a major cause of hair-cracks.

Mr. J. WOOLMAN (The Brown-Firth Research Laboratories, Sheffield): My own opinion is similar to that of Mr. Russell that hydrogen is not the fundamental cause of hair-line cracks. The fundamental cause is the generation of excessive local stresses sufficient to cause rupture of the steel, and hydrogen may be one factor responsible for the production of such stresses. Calculation of stresses in a homogeneous cooling mass shows that the tensile stresses resulting from the transformation change as it passes from outside to the centre are always greatest at the axis or near the outer surface, but are a minimum in the intermediate regions where hair-

<sup>1</sup> See F. Laszlo, "Tessellated Stresses," *Journal of The Iron and Steel Institute*, 1943, No. I.

line cracks are usually formed. The stresses produced in a cooling homogeneous mass, therefore, cannot by themselves cause the formation of hair-line cracks, and some superimposed stress over and above the normal cooling stresses must be present to account for the location where hair-line cracks are generally observed. Such localised stress is most likely to be produced by the presence of locally highly segregated areas which transform at a later stage than the material in their immediate vicinity. Any added element which will retard the transformation on cooling and which can segregate during the freezing of the steel could, in my opinion, account for hair-line cracks, and hydrogen is only one of these elements. Some evidence of this is provided by the white zones, considered by the authors to be austenite in character, and is evidence of lack of transformation in very localised areas. It is not necessary on this hypothesis to bring in the conception of voids, for which little or no evidence exists.

I am not clear as to the nature of the white zones, which in one part of the paper are attributed to ferrite and in another to austenite. Are these different, and what is their significance on the authors' hypothesis?

Dr. W. C. NEWELL (The Brown-Firth Research Laboratories, Sheffield): In connection with the papers on "The Formation of Hair-Line Cracks," I should like to put it to the authors that the issue as to the cause of these cracks would be much clearer if the water-quench following the hydrogen treatment could be avoided. The authors' procedure of sweeping off the hydrogen with nitrogen for 6 min. would result in a substantial loss of hydrogen from the specimens, and I would suggest that the experiment be repeated with the specimen rapidly cooled in air or hydrogen. I think that the loss of hydrogen by such a procedure would be less and the quenching in water would be avoided.

The usual method of determining the solubility of a gas is to saturate with gas under 1 atm. pressure. The authors have preferred to work in a constant-volume system and a variable pressure of 30 cm. to 40 cm. of mercury. There may be advantages in so doing, but the authors have not stated their reasons. There is certainly a disadvantage in that the pressure of saturation is variable from temperature to temperature and from sample to sample, and one would expect the quantity of gas dissolved to be somewhat dependent upon the gas pressure. The effect of temperature upon the pressure of the gas is great, as is shown on p. 185 P for the silica-blank curve, and yet the difference between this curve and those for the iron and steel samples is small. Even at 1100° C. the maximum temperature, the difference in pressure for the hydrogen solubility in iron is only 2 cm. of mercury. When it is realised that these experiments must take weeks to complete, and the comparison of pressures can only be made after such periods and reassembling of the apparatus, then



it would appear that the accuracy of the figures reported is to be questioned.

Great care was taken to maintain the temperature of the furnace constant within  $1^{\circ}\text{C}.$ , whilst at the same time the Pythagoras tube containing the specimen and filled with hydrogen had one end in the furnace and the other at room temperature. There would thus be a large temperature gradient along the tube, and there was apparently no check or control upon the temperature or cooling conditions of the room. With such a relatively large volume of gas at room temperature, the actual room temperature would be at least as important as the furnace temperature in so far as its effect upon the pressure of the system would be concerned. It does appear that the dead volume of the apparatus is needlessly large, and if this were smaller and if most of the dead space in the furnace tube were filled with an inert material, such as silica, then a greater sensitivity less influenced by room temperature would have been obtained.

On p. 186 P dealing with the nickel steel, use is made of graphite in conjunction with silica for the blank, the assumption being that the presence of 0.22 g. of graphite is equivalent to the 0.22% of carbon in the nickel steel. I question that. The reaction between hydrogen and graphite is not the same as that between hydrogen and cementite dissolved in steel. It is assumed that methane was formed by the reaction in each case, and, whilst this assumption may be correct, I think that it would have been desirable to have estimated the methane chemically before, from the small reductions in pressure obtained, the graph given in Fig. 7 for the thermal dissociation of methane was published.

On p. 187 P dealing with the determination of the volume of the apparatus, use was made of 99.9986% pure aluminium, which was partially oxidised and the increase in weight measured to 0.0001 g. This seems an elaboration to no purpose. Aluminium is not the best of materials for oxygen absorption, and super-purity material is quite unnecessary. Iron reasonably low in carbon would have served the purpose quite well.

Several references are made to gas at "N.T.P." when in reality the gas is considered at room temperature and 760 mm. of mercury. Room temperature is usually variable and about  $20^{\circ}\text{C}.$  Neglect of this point means that the volume of the apparatus is not 360 c.c., as stated, but round about 380 c.c., depending upon the room temperature at the time when the volume of the apparatus was determined.

On p. 188 P a formula is derived giving the amounts of hydrogen dissolved by the metal under the conditions employed, and the result is termed the "solubility." The solubility of a gas is usually referred to as the amount dissolved at 1 atm. pressure. I thought when I first saw the authors' figures that they must have assumed Sieverts' square-root law for the effect of their variable pressure,



but I find on checking up the graphs and the figures that no such corrections have been made. The actual correction, assuming Sieverts' law, would be of the order of 40% of the values given. It is therefore remarkable that the authors' results given in Table I. agree so well with those of other workers using 1 atm. pressure.

I am inclined to agree with the authors that hydrogen may be chemically combined with iron, and this makes it all the more desirable that hydrogen concentrations should be expressed on a weight basis as for all other elements. I know that it is becoming quite common practice to express hydrogen contents on a volume-to-weight basis, but it has little to justify it and is very misleading. The expression "cubic centimetres of gas per 100 g. of metal" does not properly express a volumetric relationship, and if this is really desired a volume-to-volume basis is to be preferred. I know from experience that it gives to many a false impression that the hydrogen is present in the metal in the gaseous state in voids or cavities—this is not so. We know that hydrogen can be taken up in considerable amounts by steel and the steel is solid. Nitrogen used to be expressed on a volume-to-weight basis until chemical evidence suggested the formation of nitrides. The similarity between the solubility curves for nitrogen and hydrogen demonstrates how desirable it is that hydrogen concentrations in iron and steel should be expressed on a weight basis.

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### JOINT CORRESPONDENCE.

(Figs. A and B = Plate XVIIA.)

Dr. N. P. ALLEN (Birmingham), referring to the paper on the solubility of hydrogen in iron and its alloys, wrote: It is encouraging to see an attempt being made to gain information on the behaviour of hydrogen in steel, in contrast to its behaviour in pure iron, which is a material with which the practical metallurgist is rarely concerned. Unfortunately the experimental methods adopted were insufficiently refined, and the conclusions are correspondingly insecure.

The authors were rightly unwilling to assume that the square-root law which governs the variation of the solubility of hydrogen with pressure in many other metals necessarily applies to iron at all temperatures and to all its alloys, but in this case they should surely have chosen experimental conditions in which the hydrogen pressure was constant, so as to avoid being misled by any unknown influence of variations of the pressure of the hydrogen upon its solubility.

The use of a blank run with graphite as a means of allowing for the presence of carbon in the steel introduced much uncertainty, for there is no guarantee that the amount of methane formed in the run with the steel would be the same as in the blank run, nor is

there any reliable method of calculating what the difference might be.

To obtain a satisfactory determination of the solubility of hydrogen in a carbon-bearing steel it is necessary (a) to maintain a constant known partial pressure of hydrogen, (b) to circulate the gases so as to keep their composition uniform, and (c) to determine the amount of methane (and other hydrocarbons) present in the gases when the steady state is reached at each temperature.

This might involve experimental complications, but the importance of the subject to the steelmaker is such that they ought to be faced.

Dr. U. R. EVANS (Cambridge University) wrote: The research described in the paper entitled "The Formation of Hair-Line Cracks.—Part I.," has greatly added to our knowledge of the damage caused by hydrogen absorption at high temperatures, and it is satisfactory to know that the hair-line cracks only occur after fairly rapid cooling through the  $Ar_1$  point, and that an ageing period is needed for their development.

Hydrogen can produce damage after absorption (a) through soaking at high temperatures, or (b) through pickling at low temperatures. If the action is similar in the two cases, help may be obtained by considering the phenomena side by side.

Pickling brittleness has sometimes been attributed to the hydrogen interfering with the *elastic* deformation of the steel. Recent results obtained by Dr. Stuart and myself<sup>1</sup> suggest that this is unlikely. We have found that the supercharging of steel with hydrogen does not seriously reduce the fatigue life if bending is confined to the elastic range, although fracture soon follows if attempts are made to bend specimens to and fro beyond the yield point. A more common view is that hydrogen interferes with the *plastic* deformation of the steel, so that fracture occurs instead of plastic flow. This is undoubtedly correct as a statement of fact, but it may still be asked why other alloying elements which oppose plastic deformation result in strengthening without serious embrittlement. Evidently the hydrogen, besides resisting plastic deformation, does something to encourage breakage.

If we make the reasonable assumption that the iron crystals will accommodate hydrogen when they are undistorted, but that there is a tendency to press out the hydrogen when deformation takes place, the facts become easily explicable. The work of Bardenheuer and Ploum,<sup>2</sup> who find that cold-working assists in the elimination of hydrogen from steel, makes this assumption extremely probable. The pressing-out of the hydrogen will develop local

<sup>1</sup> N. Stuart and U. R. Evans, "The Effect of Zinc on the Corrosion-Fatigue Life of Steel," *Journal of The Iron and Steel Institute*, 1943, No. I.

<sup>2</sup> P. Bardenheuer and H. Ploum, *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1934, vol. 16, p. 129,

pressures, and this fact will oppose the deformation, explaining why hydrogen resists plastic flow. But when once gaseous hydrogen has been produced within the metal, the vast pressures produced internally will cause the damage to spread, so that extensive rupture occurs. It is as though the metal contained a closely tamped charge of guncotton.

There is no doubt about the existence of the pressure produced internally by the hydrogen when once it has been evolved. The blisters clearly shown in the photographs of Edwards<sup>1</sup> are evidence of this. The fact that the damage occurs around the sites of inclusions is also easy to understand; inclusions will differ in thermal expansion from the metal, and also in mechanical properties, so that cavities will exist around them either after cooling or after rolling, which will give just that additional stress concentration needed to start the "explosion" when an attempt is made to bend the metal sharply.

Passing now to hydrogen introduced at high temperatures, it would seem likely that the fundamental rearrangement of atoms which accompanies passage through the  $Ar_1$  point will force out the hydrogen at incipient quenching cracks (themselves probably invisible under the microscope), and that the trouble, having started at this point, will continue to spread long after the original stimulus. For at any moment the distortion at the end of a crack will force out hydrogen from the iron crystals, and this hydrogen will develop the pressure which will cause the crack to extend further. Thus the action may be compared to an explosive train, and incipient cracks, at first invisible, may after some hours become visible.

Whether the hydrogen is introduced at high temperatures by soaking or at low temperatures by pickling, its presence will tend to transform non-destructive forces into destructive ones. Imagine, for simplicity, a spherical cavity in metal, and imagine compression applied to the top and bottom. If the cavity contains a vacuum, this will simply tend to close up the cavity, thus making the metal more sound. If the cavity contains low-pressure gas, there will be "pneumatic transmission" of pressure to the sides of the cavity, where rents will tend to appear. If the compression automatically produces hydrogen at very high pressure, this pressure will act in all directions; it will act towards the top and bottom, thus opposing the deforming forces, but it will act also towards the sides, thus causing cracking, which will propagate itself by developing fresh hydrogen as it extends.

This view has much in common with the suggestions advanced by Zapffe and Sims.<sup>2</sup>

<sup>1</sup> C. A. Edwards, *Journal of The Iron and Steel Institute*, 1924, No. II., p. 16.

<sup>2</sup> C. A. Zapffe and C. E. Sims, *American Institute of Mining and Metallurgical Engineers*, 1941, *Technical Publication No. 1307: Metals Technology*, Aug., 1941.

Mr. H. W. PINDER (Messrs. William Jessop & Sons, Ltd., Sheffield) wrote: One never doubted the potent influence that hydrogen could exert as a strong contributory factor in the formation of hair-line cracks even before the publication of this paper (Part I.), but hydrogen cannot be said to be the fundamental cause of hair-line cracks. This is proved by the fact that a steel without a phase change between  $1200^{\circ}$  and  $18^{\circ}$  C., that is, an 18/8 austenitic stainless steel, is free from hair-line cracks when treated in the manner of hydrogen-soaking and ageing described by the authors. Furthermore, it has not been established that a steel free from hydrogen and cooled under certain conditions (conditions which might occur in practice), will not contain hair-line cracks. It has been shown that steels soaked in nitrogen at  $1200^{\circ}$  C. and quenched in water were free from cracks; so is a steel soaked in air at  $1200^{\circ}$  C. and quenched in water. In the latter case this is due to the relatively large amount of austenite preserved, which will afford the martensite stress-relief by the compression of the austenite present.

A further point concerns the microstructure of the steel containing cracks, the edges of which were stated to be decarburised after the following treatment (to quote the authors, Part I., p. 198 P., sixth paragraph): "When the specimens were rapidly heated to  $300^{\circ}$  C. before sectioning it was found that white veins of ferrite formed along the cracks, as shown in Fig. 6, the matrix being a finely divided mixture of sorbite and ferrite. These veins were not found around every crack examined, particularly in steel F4, but were usually present. They were not found in steel F5 which was tempered at  $220^{\circ}$  C., but appeared in a similar specimen tempered at  $310^{\circ}$  C. Furthermore, no such veins occurred in specimens of any of the steels examined if the heating to the tempering temperature was slow. Indeed, in order to be sure of obtaining these white veins of ferrite around the cracks, the specimen was placed in a furnace which was already at  $700^{\circ}$  C."

It is difficult to conceive how decarburisation could occur in such a short time with dry atomic hydrogen, the relative pressure of which would be low, especially in view of the fact that Inglis,<sup>1</sup> 1933, showed that hydrogen stored in tubes under a pressure of 250 atm. at  $300^{\circ}$  C. for 8000 hr. did not decarburise nickel-chromium-molybdenum steel.

Dr. T. SWINDEN (Member of Council; The United Steel Companies, Ltd., Stocksbridge, near Sheffield) wrote: No one can dispute the value of these papers on hair-line cracks. The original terms of reference, namely, to check the experiments of Musatti and Reggiori, have been completed and the results are beyond question. They confirm the work of the Italian investigators and have extended in

<sup>1</sup> N. P. Inglis and W. Andrews, *Journal of The Iron and Steel Institute*, 1933, No. II., p. 390.



an interesting way the important subject of incubation. The fact that an incubation period was necessary was overlooked by some of the earlier investigators and misleading results arose therefrom.

I am prepared to accept that there is a *prima facie* case that hydrogen must be regarded as an important factor. I must, however, question the justification for the statement in the fourth line on p. 201 P (Part I.) that evidence was obtained that when the cracks had been formed they contained hydrogen. I suggest that this should read : " It is to be *inferred* from the following evidence and reasoning . . ." It is most important in discussing this intricate subject that we should be very precise as to what has been proved by evidence and also be explicit in wording. Thus, it is suggested that during the crack formation *at room temperature* molecular hydrogen is stored in the cracks. Now, as the authors themselves have shown, these cracks actually form and develop at room temperature (*i.e.*, incubation), and presumably the full meaning of this sentence is that at room temperature atomic hydrogen diffuses into planes of weakness of the atomic lattice, in which planes molecules of hydrogen are formed, which formation results in stresses causing cracks which are ultimately readily recognised by appropriate methods of examination.

This is clear, but the following sentence states that if heating to 300° C. is slow, this hydrogen (*i.e.*, presumably molecular hydrogen) breaks down to the atomic state, diffuses through the metal, &c. Is there any foundation for this suggestion that molecular hydrogen does in fact break down to the atomic state under these conditions ? Could we, for example, prove that molecular hydrogen, say, under considerable pressure in a confined space in steel, would diffuse out if heated under the postulated conditions ?

The penultimate paragraph (Part I.) is an attempt to correlate these laboratory experiments, carried out under conditions recognised to be far removed from those which occasion hair-line cracks, with practical experience. As such, it strikes me as being very unconvincing. It is accepted that the research proves, unquestionably to my mind, that hydrogen is a factor, and it is perhaps not unreasonable to say that the mechanism of crack formation in practice might be assumed to be similar to that outlined by the authors. It is, however, weak, in the absence of evidence, to state that, although a steel ingot may contain little or no hydrogen immediately after casting, " the possibility of hydrogen contamination during heat-treatment operations should not be overlooked." The words " heat-treatment operations " in themselves are misleading, in that these are generally applied to quenching and tempering operations, and I at least have not heard it suggested that hair-line cracks are formed from otherwise crack-free material during these operations.

Assuming, however, that the authors refer to the reheating of ingots and/or billets for rolling or forging, there is no evidence of an



increase in hydrogen content, and it is difficult to formulate any hypothesis by which this should be so. Such evidence as we have on this subject is quite definitely in the direction of showing that the hydrogen content is at the maximum immediately after casting, and that this is reduced during further manipulation or on allowing the cast pit sample to stand at atmospheric temperature.

We are hoping to obtain considerably more data on the actual hydrogen content of liquid steel immediately prior to casting, and these data should provide some direct additional information correlating hydrogen and the susceptibility to the subsequent development of hair-line cracks.

The second paper (Part II.) is also a very useful piece of academic research, and the conclusions are stated with commendable clarity. Nevertheless, accepting the hypothesis stated, we have still got to explain why, if hydrogen is the fundamental cause of hair-line cracks, basic open-hearth steel is so much more susceptible than acid open-hearth steel of identical chemical composition. This admittedly weakens the case of those who claim that hair-line cracks are essentially due to stresses set up through delayed thermal transformations on account of the presence of alloying constituents. On the other hand, however, there is no evidence, at least as yet, that basic open-hearth steel contains more hydrogen at the moment of casting than acid open-hearth steel. There is quite definite evidence that in the cold state it contains no more. Further, if hydrogen is the fundamental cause, we have still to explain why, say, a medium-carbon 1% chromium basic open-hearth steel is so badly susceptible to hair-line cracks, whereas the same steel without chromium is to all intents and purposes immune. Chromium to this extent does not depress the carbon change point (it tends to raise it), and there is no evidence that it increases the stability of the hydrogen-rich constituent. Further, the hydrogen-rich constituent is referred to as being austenitic, but it is implied, and there is some evidence to support it, that molybdenum, in the presence of other alloys, increases the susceptibility—for example, manganese-molybdenum as against plain manganese steel—yet molybdenum does not promote the formation of austenite.

These ideas are put forward for the purpose of stimulating further investigation, and the whole subject has, of course, an extremely important practical significance. We know, quite definitely, how to suppress the formation of hair-line cracks and our practice is successful. If, however, hydrogen is indeed the "fundamental cause of hair-line cracks," one would think that it would be a comparatively easy matter to immunise in the ingot stage, and, at least in my experience, this is by no means a simple matter.

Mr. A. J. K. HONEYMAN (Messrs. Colvilles, Ltd., Glasgow) wrote: I think that the authors have proved conclusively that hydrogen

is the fundamental cause of hair-line cracks, but they have introduced an unnecessary and unjustifiable complication by postulating a hydrogen-rich constituent with an extraordinary combination of properties—metastable at all temperatures; forming only on rapid cooling through the  $\gamma$ - $\alpha$  change; being austenitic in nature. The experimental facts obtained can be equally fully and much more simply explained on the basis of simple solid solution. Like other alloying elements more soluble in the liquid phase, hydrogen is subject to dendritic segregation. It is probable also that hydrogen is more soluble in the segregated portions of the steel. This is illustrated in Figs. A and B, which are typical of alloy-steel plates, the hair-line cracks occurring only in the segregated areas. Incidentally, this may also be a partial explanation of the greater tendency to hair-line cracking of material from large ingots. It also indicates that the total hydrogen in the steel is not the only factor concerned with the production of hair-line cracks; its distribution is also important, so that hair-line cracking may well occur in steels with a lower hydrogen content than when the hydrogen is introduced artificially into the steel.

Being more soluble in the  $\gamma$  phase, hydrogen *increases* the stability of austenite. But the rate of diffusion of hydrogen is very much in excess of that of any other solute, so that the  $\gamma$ - $\alpha$  transformation, in so far as it is dependent on hydrogen, is a function of time as well as of temperature. Thus, given sufficient time, the austenite may break down at any temperature, so that the hydrogen-rich austenite produces all the effects attributed to the "hydrogen-rich constituent."

The influence of composition upon susceptibility is simply one of the effect—with hydrogen—upon the  $\gamma$ - $\alpha$  change point.

The authors referred to methods for the prevention of hair-line cracks. In my experience the simplest, most effective and cheapest method is to transfer the material direct to an annealing furnace immediately after the final forging or rolling, and to transform it isothermally in the pearlite range. The most suitable temperature is that at the "nose" of the S-curve, which is independent of the finishing temperature. The minimum time for complete transformation which is essential depends upon the finishing temperature, and is, therefore, a matter of experiment and experience. High-alloy steels which cannot be so treated in a reasonable time can only be made immune by very slow cooling of the steel at one or more stages in the manufacture.

Mr. A. U. HUDDLE (Cambridge University), referring to "The Formation of Hair-Line Cracks.—Part II.," wrote: In this extremely valuable paper the authors have shown that hair-line cracks are associated with a hydrogen-rich constituent. There seems to be considerable evidence that this second phase is retained austenite, stabilised by hydrogen:

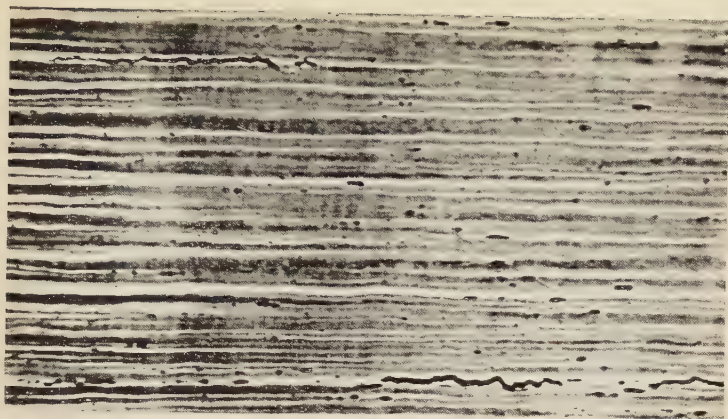


FIG. A.—Length Test.

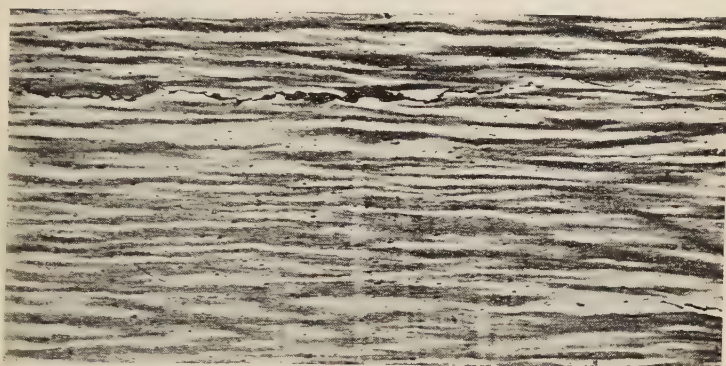


FIG. B.—Cross Test.

FIGS. A and B.—Hair-Line Cracks in Rolled Chromium-Molybdenum Steel Plate. Etched in Rosenhain and Houghton's reagent.  $\times 20$  (reduced to half-size linear in reproduction). (See Honeyman's contribution.)



FIG. C.—4S11 Steel, hydrogen-soaked at  $1150^{\circ}\text{C}$ ., air-cooled to  $330^{\circ}\text{C}$ ., then water-quenched. Left, unaged; right, aged for 1 week before sectioning. (See Authors' reply.)

[Discussion on Hair-Line Cracks.  
To face p. 262 p.]



FIG. D.—4S11 Steel, hydrogen-soaked at 1150° C. air-cooled to room temperature.  
*Left, unaged; right, aged for 1 week before sectioning.*



FIG. E.—4S11 Steel, hydrogen-soaked at 1150° C., quenched in lead-bath at 650° C., brine-quenched after holding at 650° C. for (a) 20 min., (b) 1 hr., (c) 3 hr. Vickers diamond hardness: (a) 430, (b) 417, (c) 481.

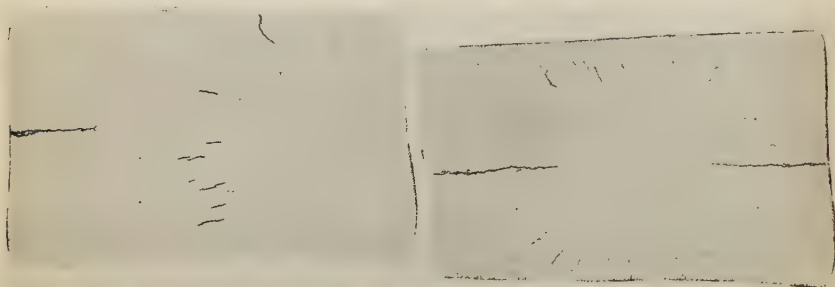


FIG. F.—4S11 Steel, hydrogen-soaked at 1150° C.  
*Left, forged and air-cooled; right, forged and quenched from 700° C.*

(See Authors' reply.)



(a) The microconstituent resembles austenite on etching in alcoholic nitric and cupric reagents, as the authors have found.

(b) Houdremont and Heller have recently shown that hydrogen acts as a carbide stabiliser in the same way as manganese and chromium.<sup>1</sup> Probably it would also resemble manganese and chromium in aiding the retention of austenite, as the authors suggest on p. 241 p.

(c) Hydrogen can be taken up in the interstices of the  $\gamma$ -iron lattice.<sup>2</sup> It is much less soluble in  $\alpha$ -iron.<sup>3</sup>

(d) The larger the grain size the greater is the amount of retained austenite.<sup>4</sup>

If it is assumed that the hydrogen-rich constituent is retained austenite supersaturated with hydrogen, the following explanation can be given to the facts observed experimentally :

(1) Hair-line cracks produced on ageing are due to the gradual passage of hydrogen from the austenite, until—in the absence of sufficient stabiliser—the austenite changes to martensite, which cannot hold the hydrogen already present, so that it is expelled under great pressure.

(2) Hair-line cracks produced on heating are also due to the transformation of austenite into martensite. This is known to occur at lower temperatures for low-carbon austenite than for high-carbon austenite,<sup>4</sup> which explains the authors' observations on the *D* series that the low-temperature hydrogen-evolution peak rises with carbon content.

(3) An almost equal volume of hydrogen is evolved from all specimens soaked at 1200° C. This is due to the rapid attainment of equilibrium between hydrogen and steel at 1200° C.

(4) The variation in cracks caused by different periods of soaking at 1200° C. is due to the increase in grain size of the steel with time at this temperature, this aiding the retention of austenite (*see above*), which leads to hair-line cracking on either ageing or heating.

(5) In the presence of applied stress, the softer austenite situated at the martensite grain boundaries (*see Fig. 40*) is first deformed and transformed into martensite, which cannot hold the hydrogen, and suffers cracking, leading to the brittleness observed by several investigators.

(6) Steels containing elements favourable to the retention of austenite, which can subsequently decompose, are susceptible to hair-line cracking.

<sup>1</sup> E. Houdremont and P. A. Heller, *Stahl und Eisen*, 1941, vol. 61, p. 756.  
*See also* D. W. Rudorf, *Metallurgia*, 1942, vol. 25, Apr., p. 182.

<sup>2</sup> Sir Wm. Bragg, *Journal of The Iron and Steel Institute*, 1921, No. I., p. 326.

<sup>3</sup> R. M. Parke, *American Society for Metals, Metals Handbook*, 1939, p. 356.

<sup>4</sup> Sir Harold Carpenter and J. M. Robertson, "Metals," vol. II., chapters XI. to XIII. London, 1939.



In a word, hair-line cracks are attributable to *the difference of solubility of hydrogen in retained austenite and in its decomposition products.*

Mr. H. O. Howson (Sheffield), wrote : The research described in the paper on " The Formation of Hair-Line Cracks.—Part II." lends additional confirmation to the viewpoint that hair-line cracks may be produced as a result of the combination of thermal stress and hydrogen treatment.

Undoubtedly, some of the discontinuities illustrated may be regarded as typical hair-line cracks, but criticism may be levelled at the nature of some of the defects shown. The magnetic method is of great sensitivity when performed on a specimen with ground surfaces, and cracks having a measured depth of 0.003 in. and an estimated width of 0.0005 in. are readily discovered. Hair-line cracks in commercial steels are usually detectable in this manner, and added confirmation may be obtained by etching with 10% nitric acid in the cold. Boiling in hydrochloric acid (of unspecified strength) for 2 hr. is rather a violent etch, and the possibility arises that some of the defects illustrated are due to the use of the over-powerful etching reagent, and may not be considered to have existed as original discontinuities. There is no description of any specimen after fracture showing the bright " flake " appearance so typical of hair-line cracks.

It is difficult to conclude how, if hydrochloric acid successfully reveals the macrostructure, the course of the cracks may be assessed as intercrystalline or transcrystalline. Surely an etch for developing the microstructure, such as nitric acid or picric acid, is necessitated ?

The retention of austenite after the rapid quenching of specimens from a high temperature has been the subject of considerable study, and the theory advanced by the authors that the hydrogen in such specimens is not dispersed uniformly throughout the steels, but is confined to the austenitic constituent, is very interesting. Presumably the hydrogen is diffused uniformly through the steel at temperatures higher than the upper critical point. Is it possible for the authors to outline the mechanism of the change by which the hydrogen diffuses completely into one sparsely distributed constituent, with the rapidity required under conditions of high cooling velocity ? It may also be stated that cracks of the hair-line type occur in rails cooled in air. In this instance, the possibility of the retention of austenite is remote.

The effect of heating retained austenite is the production of troostite or martensite ; no evidence of the formation of any such constituent is shown in Figs. 45, 46 and 47. The white hydrogen-rich filaments are stated to occur generally at the grain boundaries, and the hydrogen liberated on ageing diffuses into voids and there develops disruptive pressures. One concludes that as diffusion at

atmospheric temperature is slow, the generation of such pressures would tend to be at the grain boundaries. This would necessitate intercrystalline rupture, a condition which cannot be demonstrated in the hair-line cracks found in practice. Frequently, but not invariably, in the examination of large forgings, hair-line cracks are found associated with inclusions and abnormal metallic segregations, a significant factor in considering their origin.

Reference is made in the paper to the work of Honda in connection with the study of hair-line cracks, but the researches of Sims and Zapffe, as described in various American journals, are not mentioned. These investigators advance the concept of a "block" structure in steels, and suggest that hydrogen is occluded under high pressure in "interblock disjunctions." The resultant pressure of the hydrogen is exerted triaxially, resulting in the marked embrittlement of material containing an excessive amount of hydrogen. The superimposing of cooling stresses, particularly those resulting from the austenite-to-martensite transformation, produces an increase in internal pressure sufficient to overcome locally the cohesion of the steel. Fracture follows the surfaces of the unit "blocks," resulting in the well-known "flaky" appearance of the discontinuity. Hydrogen tends to concentrate in the locality of non-metallic inclusions, resulting in the association of these particles with hair-line cracks and similar hydrogen-embrittlement phenomena. It is submitted that this theory merits further consideration, as the appearance and occurrence of hair-line cracks are explained in a very conclusive manner.

The authors are to be congratulated on the development of such excellent apparatus for determining the rate of liberation of occluded hydrogen. This marks the commencement of a quantitative study of a subject previously approached in an entirely empirical fashion. I might suggest that useful work could be carried out in comparing the ductility of steels after hydrogen treatment under specified conditions.

Mr. T. F. RUSSELL (English Steel Corporation, Ltd., Sheffield) wrote: In Part II. of the paper on hair-line cracks the authors correctly state that during the determination of hydrogen by heating, reactions will occur which involve carbon, hydrogen and oxygen. The main products of the reactions are carbon monoxide, methane and water vapour, and the hydrogen in the latter is lost to the final analysis. It would be equally true to say that the composition of the gases varies with temperature. For this reason, and others, I think it would add interest to the paper if Figs. 9 to 14 could be recalculated and graphed in the form temperature against volume of gas at N.T.P. evolved per degree rise in temperature. Although it may not be possible to do this strictly accurately, a close approximation could probably be obtained as follows: If a mass of gas  $m$  is at uniform temperature  $T^\circ$  K. and under a pressure  $P$  and of volume  $V$ , then  $PV/T = \frac{1}{2} Rm$ , where  $R$  is the gas constant. Simi-

larly, if the mass, pressure and temperature be increased and the volume kept constant, then :

$$\frac{(P + \Delta P)V}{(T + \Delta T)} = \frac{R}{2} (m + \Delta m),$$

and by division :

$$\frac{P + \Delta P}{P} \cdot \frac{T}{T + \Delta T} = \frac{m + \Delta m}{m} = \frac{v + \Delta v}{v} \quad . \quad . \quad . \quad (A)$$

where  $v$  is the volume of gas at N.T.P.

From this it is seen that if  $\Delta T$  is so small that  $T/(T + \Delta T)$  is approximately equal to 1; then :

$$\frac{\Delta P}{P} = \frac{\Delta m}{m} = \frac{\Delta v}{v},$$

or, at constant temperature,  $P/v$  is a constant and the increase in volume at N.T.P. is proportional to the increase in pressure, as is apparently assumed by the authors.

In the experiment, however,  $T/(T + \Delta T)$  varies from 1 to about  $\frac{1}{5}$ , and the substitution of its correct value in equation (A) to determine the value of  $\Delta v$  for a rise in temperature  $\Delta T$  would probably alter the "rate of evolution" curves quite appreciably. As the temperature of the apparatus is not uniform the value of  $T/(T + \Delta T)$  cannot be taken from the temperatures of the test-piece, but it is suggested that its value could be obtained to a fair degree of accuracy from the temperature/pressure calibration curve for the apparatus. Such temperature/temperature-rate-of-evolution curves would, by integration, give the volume of gas at N.P.T. obtained over any particular range of temperature, and a comparison of the total volume obtained by this method and the volume after cooling to atmospheric temperature *may* give some indication of the amount of water vapour formed during the course of the experiment.

As it is extremely probable that the percentage volume of each constituent gas in the mixture will change when the temperature changes, it seems well worth while to compare a temperature/pressure curve, taken with a permanent gas like hydrogen with one taken with a mixture of gases such as is obtained in the extraction apparatus, to see to what extent the peaks on the authors' evolution curves are influenced by the reactions between the gases themselves.

The exact interpretation of gas-evolution curves is made more difficult still by the fact that the form of the curves will be profoundly altered by the rate at which the specimen is heated.

Dr. T. P. HOAR (Metallurgical Laboratories, Cambridge) wrote : With most of the authors' interpretations of their very important experiments I am in complete agreement, but I question some of their remarks concerning the postulated hydrogen-rich constituent. They say (Part II., p. 238 P) that the constituent "must be regarded as metastable at all temperatures, and for a given steel, its stability

will depend on the amount of hydrogen in solid solution in the steel." This is not in accord with the established principles of thermodynamics and kinetics. A metastable substance depends for its *apparent* stability on its very slow rate of change into the form truly stable under the prevailing conditions; and this apparent stability, as measured by the slow rate of change, is in no way influenced by the concentration or active mass of the stable form resulting from the change. Thus, the suggested "rapid breakdown" of the constituent on ageing could not possibly be influenced by the diminished amount of hydrogen in true solution. A more rapid rate of breakdown on heating would, of course, be expected, but, again, this rate would not be affected by the amount of hydrogen in true solution.

Is it not possible that a mechanism akin to that of an explosion or chain reaction might serve to explain the sudden release of gas after ageing or heating? During ageing or heating, hydrogen in solid solution might be expected to diffuse to the surfaces of closed rifts and voids, there becoming molecular and setting up high pressures on desorption, as suggested many years ago by Edwards and others. The pressure in any one void having become high enough, splitting of the void could occur, with formation of a hair-line crack and release of gas to the surrounding atmosphere; and this same mechanical disturbance could, one might suppose, set off further splitting of neighbouring voids in which the pressure had not yet risen sufficiently to give spontaneous cracking. In this way a sudden release of much gas could, I think, find ready explanation.

Mr. G. PARKIN (Messrs. Ed. Pryor & Son, Ltd., Sheffield) wrote: Whilst these comments are largely concerned with Parts I. and II. of the hair-line crack papers, the importance of the work on hydrogen solubility determinations is not forgotten. The sponsors and authors of the whole work are to be congratulated on achieving recognition for what the writer considers to be a major steel problem. No one can doubt the technical and economic importance of hair-line cracks, particularly when the time, cost and relative uncertainty of commercial immunisation treatments are remembered. A search of the literature relevant to hair-line cracks reveals that much useful work has been done in America, Germany and other countries, but full recognition of the problem in Britain appears to be overdue, and for this reason the present papers are welcomed.

There is still a tendency to evaluate the problem of hair-line cracks in terms of a single factor. Thus, we have the hydrogen theorists, the stress theorists and others. Surely it is reasonable to consider the possible factors additively and not as causes each complete within themselves. The writer believes that hair-line cracks in steels are a function of hydrogen content and stress. This stress, which may be of a complex order, and which may arise from a number of causes, is additive to any induced by the presence of hydrogen alone,



The transformation-stress theory of hair-line crack formation has had many supporters and many apparently still exist. In work done abroad, many tests were made by air- and furnace-cooling nickel-chromium steels, and it was shown that cracks developed at low temperatures some appreciable time after all transformation was completed. Klausting concluded that some relation exists between cracking or flaking and transformation, pointing out that cracking does not occur during transformation but after an incubation period, which he attributes to the slow diffusion of hydrogen. It would be interesting to learn whether the authors believe in this relationship, in view of the austenite retention attendant upon the water-quenching of their specimens and the possible effects of ageing. Is it possible, for example, that the evolution of hydrogen indicates the initiation of transformation, which might perhaps be measured by magnetic methods?

Though many workers have proved, at least to their own satisfaction, that transformation stress, even when amplified by drastic heat treatment and ageing, is insufficient in itself to produce cracking, it is reasonable to ask whether hydrogen as a single factor can cause hair-line cracking in a metal which exhibits no transformation on cooling. It is generally acknowledged that only certain classes of steels are susceptible to hair-line cracking, and it might be of interest to apply the hydrogen treatment to chemically pure iron and austenitic steel samples. In the absence of hardening or age-hardening elements, the allotropic change in iron should be the only stress-producing factor, irrespective of quenching stresses arising from the shape and size of the specimen. Thus, if a pure iron sample were brine-quenched and aged, the mass might be initially supersaturated with hydrogen, but any subsequent evolution during ageing could take place in the absence of transformation stress. It might be found that the hydrogen present is insufficient to rupture otherwise stress-free metal at normal temperatures.

Similarly, tests might be conducted by hydrogen-treating steels which are wholly austenitic at room temperature. The possibility of  $\delta$ -phase retention by quenching from high temperatures must be remembered, but it would be interesting to see if hair-line cracks developed in quenched austenitic steels aged at room temperature. A series of specimens submitted to the same hydrogen treatment could then be aged at sub-zero temperatures (say,  $-60^{\circ}$  to  $-70^{\circ}$  C.) and the possible incidence of flakes observed. The austenitic manganese and 18/8 type steels would lend themselves to such experiments. The major point of these suggestions is that, if transformation stress cannot be dissociated from hair-line cracking, then immunisation treatments would preferably involve consideration of steel transformation characteristics. These would include the change in hydrogen solubility accompanying the  $\gamma$ - $\alpha$  phase change, which is explainable by Bragg's observation that in the face-centred cubic lattice there exists a "hole" in the centre of the cube

considerably larger than any free space in the body-centred cubic lattice. It is of interest to note that Esser believes that, for the removal of hydrogen from iron, repeated heating through the critical range favours gas evolution by reason of atomic rearrangements during transformation. Again, Bennek and Klotzbach suggest that annealing just below the transformation temperature, between hot-working operations, reduces the incidence of hair-line cracks in alloy steels. These views are in line with the authors' comment on the removal of hydrogen by heat treatment within the  $\alpha$  range, at temperatures high enough to avoid trouble from methane formation, which the writer agrees is an important factor in hair-line crack recurrence. It might be worth while to test the effect of cooling susceptible steels isothermally, having due regard to their particular S or time-temperature-transformation curves.

The second point of interest concerns the hydrogen-rich constituent. The authors state that the hydrogen causing the cracks is not held in solid solution but is temporarily held as a hydrogen-rich constituent. It is gratifying, at least to the writer, to see that no suggestion of iron hydrides is made. No convincing evidence has yet been advanced for the existence of such compounds, but there is quite good evidence against them. The solubility of hydrogen in iron increases with temperature, in contrast to metals like palladium and tantalum, which form definite hydrides that dissociate at particular temperatures. Molten iron saturated with hydrogen contains only one atom of the gas to about 2,000 iron atoms, and the ratio at room temperature is less than 1 to 2,000,000. Again, no compound of iron and hydrogen possessing a definite structure has yet been identified; X-ray examination of iron-hydrogen alloys reveals distortion of the iron lattice, but the diffraction lines are always diffuse. If the hydrogen in the rich constituent is neither in solid solution nor chemically combined, at least with the iron, its nature is certainly of problematical order. If the localised hydrogen enrichment occurs through rejection of the gas by the matrix, due to lowered solubility, would the authors say that the constituent contains more hydrogen than the austenite saturated at high temperature? Further, why should the constituent possess any characteristics of even an unstable austenite if the hydrogen is not in solid solution? Is it not feasible that a super-saturated solid solution can occur locally? Such a phase would undoubtedly show a ready tendency to break down, even under conditions of negligible temperature or pressure change.

Many suggestions for further work might be made, but it would be of interest to know whether the authors' method for measuring the volume of evolved hydrogen from treated specimens could be modified and extended to include pressure measurements. Further, if it were feasible to age quenched samples under a high positive hydrogen pressure one should theoretically be able to produce hair-line cracks at the surface.

Although there are certain effects of hydrogen which have not been considered, and for which explanations have not yet been forthcoming (*see* the work of Ham, Esser and Cornelius), there can be little doubt about the value and importance of the present papers, and it is hoped that the authors will receive every encouragement to continue the work. As they have indicated, there is a great deal to be done arising from the findings so far obtained, and this is distinct from a consideration of steelmaking practice as it affects the incidence of hair-line cracks.

### *AUTHORS' REPLY.*

(Figs. C to F = Plates XVIIA. and XVIIIB.)

In reply the AUTHORS wrote : We are grateful to the many people who have contributed to the discussion either verbally or by correspondence. In view of the fact that the papers under discussion appear to be the first on the subject published by a British Journal it is not surprising that the opinions expressed by the contributors are so widely divergent. We are surprised that so many of our industrial friends still cling to their stress theories, apparently ignoring any new facts which may be presented to them. At the same time many helpful comments and suggestions have been made, and we wish to express our appreciation of these.

In reply to Dr. Hatfield we would point out that the work described in our papers was undertaken at the request of the Hair-line Crack Sub-Committee, of which he is Chairman, with the specific object of proving or disproving the work of Musatti and Reggiori. This necessitated the experiments being carried out in the presence of the "excessive amounts of hydrogen" to which he now objects. At the beginning of the work we were unprejudiced and willing to accept any theory which would explain the experimental results, but as the work developed the rôle played by hydrogen in the formation of hair-line cracks was seen to be vitally important.

The fact that Dr. Hatfield and Mr. Dawson do not agree on the order of susceptibility of various steels appears to indicate the necessity for systematic investigation under controlled conditions. Such conditions are difficult to obtain in a production plant, owing to the many operations involved, and this is particularly true when, as we believe, the most important factor is a gas—hydrogen—and when every operation can influence the amount of hydrogen retained in the steel.

As a matter of interest we should like to know how Dr. Hatfield explains the difference between his results and those obtained by Mr. Dawson in terms of transformation stresses, which we understand to be determined by the composition of the steel under the same conditions of cooling.

Of the "real facts" put forward by Dr. Hatfield, we are not in a

position to question his statement that only a very small proportion of steel suffers from hair-line cracks even when no special treatment has been given to the steel, but we do doubt the value of the hydrogen figures which he quotes for commercial steels. The hydrogen values obtained by the vacuum fusion or normal vacuum-heating methods depend upon the size of the specimen and the time which has elapsed since the steel was cast. Given sufficient time, all hydrogen will escape from the steel to the atmosphere except that which has become trapped in small internal holes. The time element is important in all cases, but particularly so with the very small samples normally used for hydrogen estimations.

We are glad that Dr. Hatfield is able to confirm the view that molten steel may contain large quantities of hydrogen, but our results using larger specimens cut from relatively small ingots and examined within a few hours of casting, indicate that large quantities of hydrogen are retained in the solid steel; indeed, we have found that, immediately after casting and cooling, more hydrogen may be present in the ingot than can be introduced by high-temperature hydrogen treatment.

Hair-line cracks can be produced in most low-alloy steels by soaking in hydrogen at high temperature followed by water-quenching or air-cooling according to the size of the specimen, but in similar nitrogen-treated specimens no such defects occur, although there is no reason to suppose that the transformation stresses are different in the two cases.

With regard to the suggestion that carbon steels do not suffer from hair-line cracks and that this is due to the fact that the transformation takes place when the steel is in a plastic state, we would refer to American rail steel which is very susceptible to "shatter cracks" and which gives internal cracks after hydrogen treatment, although the transformation occurs at about  $680^{\circ}$  C. on cooling.

We thank Mr. Burton for his constructive criticism and regret that it is not possible to carry out all the experiments which he suggests. We have not, as yet, found a refractory tube which will withstand soaking in hydrogen at a high temperature and remain vacuum-tight during relatively rapid cooling. With small specimens the rates of cooling which are possible within the refractory tube are such that practically all the gas is evolved on cooling, and no cracks can be obtained under these conditions.

With regard to Mr. Burton's second suggestion, we hope to carry out experiments along these lines in the near future when suitable steels are available.

We agree with Mr. Oliver that hydrogen-rich austenite would go a long way to explain the experimental facts. Indeed, we have said that the hydrogen-rich complex may be austenitic in nature, and it is clear that all the properties which we have postulated have been those of retained austenite rich in hydrogen.

We have said that the hydrogen-rich constituent should be



regarded as a reservoir from which hydrogen would subsequently be released to form cracks in positions determined, to a large extent, by the stresses already existing in the steel. On this view, the cracks may or may not be in the same positions as the hydrogen-rich constituents, but we believe all the cracks to be of essentially the same origin.

The suggestion that hydrogen might be in solution as protons is interesting and may have a bearing on the formation and stability of the hydrogen-rich austenite.

Any cavity which is large enough to accommodate a few molecules of hydrogen could serve as an initial void, and there must be many cavities of this type in steel. The type due to misfit between mosaic fragments is probably quite suitable, and, in addition, the fact that some of the cracks are transcrystalline may be due to these misfits making it easier for the cracks to be propagated across the crystal than along the grain boundary.

Dr. Sarjant is right in stressing the relative importance of size of material and gas content under industrial and laboratory conditions.

The results reported in Table VIII. on p. 225 p are a true statement of fact, but are apt to be misleading if used to deduce the effect upon crack formation of slow cooling through  $Ar_1$  followed by rapid cooling to room temperature. The four specimens referred to in Table VIII. were heated for evolution immediately after quenching, and our experience had shown that specimens quenched from above  $Ar_1$  invariably developed cracks if such cracks would have been produced after ageing at room temperature. Experiments since carried out, however, show that this is not true of specimens quenched from below  $Ar_1$ . In this case heating immediately after quenching produces no cracks, whereas ageing at room temperature results in crack formation. This new result removes the apparent anomalies from Table VIII. and answers the point raised by Dr. Sarjant. It is illustrated by Fig. C, which shows the appearance of specimens of 4S11 steel quenched from  $330^\circ\text{C}$ . with and without ageing. The idea that in air-cooled specimens cracks are normally formed in the neighbourhood of  $200^\circ\text{C}$ . is not supported by the results illustrated in Fig. D. A hydrogen-treated specimen of 4S11 steel sectioned immediately after air-cooling showed a single crack, but after ageing for a week the cracks were numerous. It is interesting to note that during the ageing period the air-cooled specimen evolved the same amount of gas as that quenched from below  $Ar_1$ , namely, 2.5 c.c. per 100 g. in a week. From the appearance of the evolution curves obtained at room temperature, it would seem that the incubation period in both cases is of the order of 24 hr.

Dr. Sarjant is wrong in stating that we have postulated the formation of chemical compounds. We have referred to a hydrogen-rich constituent or a hydrogen-rich complex austenitic in nature. Moreover, there should be more internal space in the  $\alpha$  state than in the close-packed  $\gamma$  lattice, and it may be that this accounts for the higher rates of diffusion in the  $\alpha$  form.

We should be very interested to have a more detailed account of the manner in which Dr. Sarjant would explain hair-line crack formation in terms of internally adsorbed films of hydrogen, since hydrogen-embrittlement and hair-line crack formation appear to be different phenomena.

We have carried out dilatometric measurements during hydrogen soaking, cooling and reheating, but no useful information was obtained.

It is true, as Dr. Gregory points out, that our results show that nickel increases the solubility of hydrogen in steel very considerably in both the  $\alpha$  and the  $\gamma$  forms, but this is a well-known fact.

It seems impossible to explain crack formation in terms of the volume change at the  $\gamma$ - $\alpha$  transformation, in view of the fact that no cracks are observed in nitrogen-treated specimens. According to the views which we have expressed, hydrogen should not bring about crack formation in the absence of allotropy, and this is supported by the fact that pure nickel soaked in hydrogen at 1200° C. for a week, water-quenched and aged showed no defects whatsoever, although the hydrogen content was larger than in comparable steel specimens. It is also of some interest that a similarly treated nickel specimen evolved no gas at room temperature.

With regard to the conical specimen, the fact that no cracks were observed in the smaller sections is probably to be attributed to the fact that hydrogen could escape more readily from these parts.

We can assure Dr. Gregory that deep-etching does not produce cracks under our conditions. For example, we have never observed cracks in deep-etched nitrogen-treated specimens, and the magnetic crack detector or electrolytic etching reveal identical features in the majority of cases.

Mr. Russell has attempted to explain the difference between the effect of hydrogen- and nitrogen-soaking in terms of the active nature of hydrogen at high temperatures, whereby small voids are formed, weakening the material in their neighbourhood and causing a local concentration of body stress. Based on this argument, once the voids have been created, the steel should be susceptible to cracks even in the absence of hydrogen. We have, therefore, put this theory to the test in the following manner: A specimen of 4S11 steel, 3 in. long by 4½ in. in dia., was soaked in hydrogen at 1050° C. for one week and cooled in air to 300° C. in 24 hr., thus allowing the bulk of the hydrogen to escape. The specimen was then cooled to room temperature and subsequently soaked in nitrogen at 1050° C. for one week, after which it was allowed to cool naturally in air. The specimen was aged for a week, but no cracks were observed, although hydrogen-treated specimens of this size never failed to show cracks after air-cooling.

Transformation stresses can probably be assessed at their true value in respect of hair-crack formation as a result of the following experiment: Six specimens of 4S11 steel, 1 in. long by 1 in. in dia., were soaked in hydrogen for four days at 1150° C. and quenched into

a large-capacity lead-bath maintained at  $650^{\circ}\text{C}$ . Specimens were removed from the lead-bath and immediately quenched in brine after 5 min., 20 min., 1 hr., 3 hr., 9 hr. and 24 hr., respectively. The first two specimens showed many internal cracks on sectioning, the third specimen had a single radial crack extending to the surface, whilst the remainder were completely free from such defects. The specimens had *not* transformed even after 24 hr. at  $650^{\circ}\text{C}$ .; indeed, the hardness increased with time of soaking up to 3 hr. These results are illustrated in Fig. E, and prove conclusively that, in this case for certain, hydrogen is the fundamental cause of cracks, since, in the

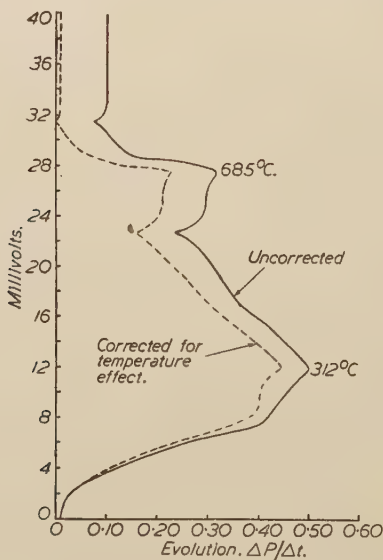


FIG. G.—4S11C Steel, soaked in hydrogen for 70 hr. at  $1200^{\circ}\text{C}$ . Evolution curve corrected for expansion due to rise in temperature.

absence of hydrogen, the transformation stresses, although severe, are incapable of producing cracks.

We should like to know the nature of the evidence which would convince Mr. Russell that hydrogen is essential to hair-crack formation, and also how Mr. Russell would attempt to explain the results of the experiments which we have now described.

Mr. Russell has, like many others, been misled by the hydrogen values which are quoted for commercial steels, and we would refer him to our reply to Dr. Hatfield's contribution.

We realised that there was a temperature effect superimposed upon the gas evolution during our heating experiments, but our results suggested that this effect was small, and would not affect the general shape of the curve. We have since calibrated the apparatus

with hydrogen in the manner suggested by Mr. Russell and applied the results to correct the curve for the unaged specimen of Fig. 11 of the paper. The original and corrected curves are shown in Fig. G, from which it will be seen that the general shape of the curve is unaffected, and our deductions are, therefore, still valid. With regard to the suggestion that the peaks on the curves may be due to reaction between the gases in the tube, it should be borne in mind that even after cooling to room temperature the gas contains about 80% of hydrogen, and, therefore, any such reaction and the effect would be confined to the remaining 20% and would be too small to account for the peaks observed. In addition, it should be remembered that the most important peaks occur only in curves corresponding to specimens in which cracks develop during heating for evolution.

Many of the points made in reply to Mr. Russell with regard to stresses apply also to Mr. Woolman's contribution. We do not suggest that stresses existing in the steel are of no importance in deciding the *position of occurrence* of the cracks, and we agree with Mr. Woolman that such stresses by themselves cannot lead to the formation of hair-line cracks.

If segregation were as important as Mr. Woolman suggests, the distribution of the cracks should be determined by the distribution of segregates and independent of the conditions of cooling. The following experiments do not support Mr. Woolman's view: (a) When hydrogen-treated specimens are (1) water-quenched and aged, the cracks are in radial distribution, (2) air-cooled and aged, the cracks are deep-seated, more or less random in direction and fewer in number, (3) up-ended and forged to about 30% reduction and air-cooled, the cracks are deep-seated and perpendicular to the direction of working, although the original flow-lines of the rolled bar persist in the other direction; (b) similar specimens water-quenched from 700° C., when forging ceased, gave radial cracks, Fig. F. Although in particular cases hair-line cracks and segregates may coincide, and so give the impression that segregation is all-important in crack formation, the above experiments show that segregation is, at the most, a contributory factor.

As far as the nature of the white zones is concerned, we would request Mr. Woolman to read the papers once more, as we think that no reasonable cause for confusion exists.

Dr. Newell's statement that sweeping off the hydrogen with nitrogen for 6 min. would result in a substantial loss of hydrogen from the specimen does not agree with our experience. We have several times quenched specimens direct from hydrogen, but the hydrogen content of the specimen agreed with that of specimens treated in the normal manner. Further, if Dr. Newell will refer to Table VIII. (p. 225 P) he will see that during cooling in air from 1200° to 520° C. in 8 min. a specimen of 4S11 steel lost practically no hydrogen.



With regard to the determination of the solubility of hydrogen in iron and its alloys, we are fully aware that the usual method is to saturate the specimen with gas under 1 atm. pressure. Before the discussion on these papers occurred, and also when the paper was introduced, we modified the text to draw attention to (1) the variation in pressure of saturation with temperature and specimen, (2) the fact that our figures were apparently higher than those of other workers and we gave the probable reasons for this, and (3) the point that the work was undertaken because of its implication with regard to hair-line crack formation, and, therefore, our primary interest was in the manner in which hydrogen is evolved on cooling.

Dr. Newell's criticism based on the time which elapses between the beginning and end of an experiment, and upon the possible variation in room temperature are both answered by the statement which we made on p. 184 P to the effect that the blank curve was checked to ensure that no spurious effects were observed. As a matter of fact, this second blank curve was obtained over a month after the first one and identical results were obtained. In the constant-pressure method it is essential that the dead space be reduced to the absolute minimum, but errors due to dead space are eliminated in the constant-volume method by taking a calibration curve. The only error which this method will not overcome is that due to possible variations in atmospheric temperature. These are small in the laboratory in question and we have not been able to detect pressure changes due to this effect, as illustrated by the repeated blank curves.

With regard to the experiments on the nickel steel, it is quite true that it would be better to use  $\text{Fe}_3\text{C}$  instead of graphite, but this is not practicable. We realised that the graphite could give us only an approximate correction for the methane effect, but believe that the error which results from this approximation is small under our experimental conditions. Indeed, if it be assumed that, under our conditions, the methane values for  $\text{Fe}_3\text{C}$  bear the same relationship to the methane values for carbon, as was the case in Schenck's experiments, then it can be shown that the error due to this additional amount of methane, which was considered as hydrogen in our work, leads to solubility values which are too high by a maximum amount of 5% at 600° C. On the other hand, the formation of extra methane in this manner would reduce the partial pressure of the hydrogen, and this would result in a lowering of the solubility value obtained. If it be assumed, for the purpose of a first approximation, that Sievert's law applies over this range of pressures, then the apparent solubility values will be too low by an amount which is almost exactly equal and opposite to the error due to extra methane taken as hydrogen.

Surely it is better to attempt to determine solubility in steel, even approximately, than to be satisfied with work carried out on special alloys which have no practical importance. The most

important feature of the solubility curve for the nickel steel is the sluggish nature of the transformation in the presence of hydrogen, and our most recent results on the effect of hydrogen upon the isothermal transformation of steel, as yet unpublished, are in keeping with this observation deduced from the solubility curve.

The suggestion that methane should be determined chemically is unsound, since it would lead to errors due to changes in the pressure and composition of the gas in contact with the specimen.

The purity of the aluminium was given as a statement of fact and not as a suggestion that such purity was essential. Nevertheless, as previously pointed out to Dr. Newell, the steel filings which he suggested in the verbal discussion are quite unsuitable, in view of the possible reaction between surface and internal oxides and carbon, leading to the formation of carbon monoxide. Dr. Newell now suggests "iron reasonably low in carbon," but to obtain a suitable iron would have been much more difficult than to make use of the "super-purity" aluminium which happened to be available.

In connection with Dr. Newell's allegation that our results should be quoted for room temperature and 760 mm. of mercury, perhaps it will suffice to point out that the apparatus was calibrated in terms of one gramme-molecular weight of oxygen occupying 22.4 litres at N.T.P. The solubility values were all calculated from this calibration, according to which a change in pressure of 1 cm. of mercury would correspond to the removal of an amount of gas which would have a volume of 4.74 c.c. at N.T.P.

As already stated, our solubility values would appear to be higher than those obtained by other workers, and some of the reasons for this have been put forward in the text. We have not used Sievert's law in order to make a direct comparison with the results obtained by other workers, because, to the best of our knowledge, Sievert's law, although theoretically sound, has never been proved experimentally, except in Sievert's early researches, which he later proved to be some 50% in error.

We have at no time suggested that the hydrogen was chemically combined with iron. In expressing the hydrogen in solution as so many cubic centimetres per 100 g. we have followed the accepted practice. Owing to the small atomic weight, if the concentration of hydrogen is expressed on a weight basis it may appear too small to have any practical importance. On the other hand, to be really scientific one should advocate the use of atomic percentages, and we should be in complete agreement with such a suggestion.

We thank Dr. Allen for his constructive criticisms, and from the theoretical point of view agree with all that he has said. From the practical point of view, however, the complications of technique which he suggests would involve probably years of work, and our primary interest was in the loss of hydrogen by steel on cooling. Although, as pointed out in the reply to Dr. Newell, the use of graphite leads to what is admittedly only a first approximation to

the amount of methane formed with a steel specimen, it is interesting that the most outstanding feature of the solubility curve for the nickel steel, namely, the sluggish nature of the transformation in the presence of hydrogen, is being confirmed by the results of experiments now in progress.

We thank Dr. Evans for his interesting comparison of the effects of hydrogen introduced at high and low temperatures, respectively. To our mind the most important difference is that after high-temperature treatment the hydrogen is in solid solution, whereas low-temperature treatment, such as pickling, would appear to result in the formation of adsorbed layers of hydrogen at the grain boundaries. By prolonged cathodic treatment of standard evolution specimens at room temperature, we have succeeded in introducing hydrogen to the extent of some 3 c.c. per 100 g. The amount of gas evolved at room temperature from such a specimen is extremely small, whilst the evolution curve on heating is quite different from those obtained with hydrogen-soaked specimens, even those of comparable hydrogen content. We believe that when the hydrogen is in solution any deformation or stresses imposed on the steel will affect the rate of diffusion rather than the actual solubility, but the idea of "pressing out the hydrogen" may give a good picture of what happens when the hydrogen is occluded at the grain boundaries.

The result given in Table X. (p. 227 P) support the view that any atomic rearrangement facilitates the elimination of hydrogen from solution, but our view is that in low-alloy steels the presence of hydrogen may stabilise and retain some of the austenite. The breakdown of this austenite with the release of hydrogen at a relatively low temperature is the basis of our explanation of hair-line crack formation.

In our opinion, a phase change with its accompanying sudden drop in hydrogen solubility is essential for crack formation. The fact that, as pointed out by Mr. Pinder, 18/8 austenitic stainless steel does not give cracks after hydrogen-treatment is quite understandable on this view.

There is no evidence for supposing that less austenite is retained in water-quenched steel specimens after hydrogen-soaking than after heating in nitrogen or air, but rather the reverse, and, therefore, Mr. Pinder's suggestion of martensitic stress-relief by the compression of austenite is quite unsound.

The work of Inglis and Andrews is hardly relevant, in view of the widely differing conditions involved. An estimate of hydrogen pressure in the cracks at 300° C. based upon the width of the decarburised layer leads to a value of some 8000 atm. Moreover, from the point of view of chemical activity, the surface of a freshly formed crack can hardly be compared with that of a machined tube.

Inasmuch as the interpretation of any new experimental result always involves "inference" at some stage or other, we agree with Dr. Swinden's suggestion, but since there is, on our existing know-

ledge, no explanation of the decarburisation around the cracks other than the existence of hydrogen within them, we consider that our statement that "evidence was obtained that when the cracks had been formed, they contained hydrogen" was fully justified. Since a description of that evidence immediately followed the sentence to which Dr. Swinden objects, there should be no question of misunderstanding.

There is certainly evidence that molecular hydrogen in contact with a clean iron surface breaks down to give an adsorbed layer of atomic hydrogen. Thus, the work of Emmett and Harkness<sup>1</sup> shows that, even under atmospheric pressure, such activated adsorption is prominent from  $-100^{\circ}\text{C}$ . to about  $+400^{\circ}\text{C}$ ., being a maximum in the neighbourhood of  $100^{\circ}\text{C}$ . Activated adsorption increases with increasing pressure. The escape of molecular hydrogen from the cracks will be determined partly by activated adsorption and partly by the rate of diffusion of atomic hydrogen through the steel. Although there is evidence for a marked increase in the rate of diffusion near  $300^{\circ}\text{C}$ ., diffusion is appreciable even at lower temperatures, and shows an almost linear increase with the temperature. This is further supported by our evolution experiments.

Bearing these facts in mind, and taking into account the high hydrogen pressure which will favour the formation of methane, we believe that we have given a true picture of what happens within the cracks.

By "heat-treatment operations" we did not mean ordinary quenching and tempering treatments but were referring to any operation in which steel is soaked for a long time at a high temperature. We do not suggest that such treatments in industrial practice must necessarily introduce hydrogen into the steel, but such a "possibility" still exists and "should not be overlooked."

We agree that the fact that basic open-hearth steel is more susceptible to hair-line cracks than acid open-hearth steel of the same composition is extremely difficult to explain in terms of transformation stresses. On the other hand, a reasonable explanation can be put forward on the basis of the hydrogen theory, and we would draw Dr. Swinden's attention to the following features of the basic open-hearth process: (1) The short time of boil, (2) the large amounts of lime used, and (3) the nature and quantity of scrap employed.

Dr. Swinden's statement that "there is quite definite evidence that in the cold state basic open-hearth steel contains no more hydrogen than acid open-hearth steel of the same composition" is presumably based upon determinations made by the vacuum fusion or vacuum-heating methods. As we have said before, the specimens normally used for these methods are too small, and the importance of the time factor has normally been overlooked. Our experience

<sup>1</sup> *Journal of the American Chemical Society*, 1935, vol. 57, p. 1631.



has shown that even with a specimen 2 in. long by  $1\frac{3}{4}$  in. in dia. the loss of hydrogen in the first hour is generally of the order of 0.5 c.c. per 100 g., and with smaller specimens the relative loss is even greater. Thus, the hydrogen figures determined on small specimens weeks, or even months, after the steel was cast cannot be regarded even as an approximation to the true hydrogen content of the steel immediately after solidification.

Both chromium and molybdenum retard the rate of transformation in steel, although this does not necessarily mean that they should promote the retention of austenite to room temperature. Nevertheless, any delay in the transformation would also delay the evolution of hydrogen from the steel, and from this point of view it is conceivable that both chromium and molybdenum would favour the retention of hydrogen.

It is true that with small specimens such as can be employed in laboratory experiments the elimination of hydrogen is a relatively simple process, but with the large sections met with in industry the problem appears to be more troublesome, owing to the long times involved.

We fail to understand why Mr. Honeyman objects to our conception of a hydrogen-rich constituent, austenitic in nature, &c. The hydrogen-rich austenite retained by hydrogen, which he describes, is identical with our hydrogen-rich constituent. Mr. Honeyman said that such austenite could break down at any temperature; surely this means that it is metastable?

With regard to the effect of segregation upon hair-line crack formation, we would refer Mr. Honeyman to our reply to Mr. Woolman. The example which Mr. Honeyman gives is interesting, but it is also worthy of note that the direction of the cracks, although in segregates, is also parallel to the direction of rolling.

We are not in a position to discuss the relative merits of the various methods of industrial immunisation, but one thing does seem to be clear, namely, that the most successful methods are those which would be the most effective in the removal of hydrogen from the steel.

We thank Mr. Huddle for his helpful contribution. For the most part his views coincide with our own and we feel that he has given an excellent analysis of the conclusions justified by our experimental work.

As stated in our reply to Dr. Gregory, the cracks produced by hydrogen treatment are readily revealed by deep-etching, electrolytic etching or the Magnaflux method, and no cracks, or defects resembling cracks, are revealed by deep-etching nitrogen-treated specimens. This shows that Mr. Howson's contention that some of our cracks are produced by pickling in a constant-boiling hydrochloric acid solution is incorrect.

Hydrogen-treated specimens fractured after suitable grain refinement gave the characteristic bright "flake" appearance. In

both small and large specimens the distribution of flakes agrees with that of the cracks.

As is usual in metallographic work of this nature, macro- and micro-examinations were carried on side by side, and the inter- or transcrystalline nature of the cracks was deduced from the micro-examination.

We have not suggested that the hydrogen diffuses completely into the retained austenite, but merely that the hydrogen which cannot be retained in the  $\alpha$ -iron is concentrated in the untransformed austenite, and, in the limit, may retain this austenite to lower temperatures. Mr. Howson has apparently overlooked this possibility of the retention of austenite by hydrogen in rail steel.

The disappearance of the hydrogen-rich filaments is due to the merging of the decomposition products into the background, which has the same structure; therefore, one would not expect the appearance of troostite or martensite to be obvious around the filaments in Figs. 45, 46 and 47.

We cannot agree with Mr. Howson when he implies that our results lead to the conclusion that hair-line cracks must be inter-crystalline. For example, it has yet to be proved that the diffusion of hydrogen is easier along grain boundaries than through the metal lattice.

We are acquainted with the work of Simms and Zapffe to which Mr. Howson refers and agree with many of their conclusions, but we fail to see how their theory can account for the incubation period or for the sudden evolution of hydrogen which occurs at the end of it and which coincides with hair-crack formation.

In reply to Dr. Hoar, we believe that the hydrogen-rich constituent is austenite stabilised by hydrogen, and our results are certainly in keeping with the view that the stability of this constituent depends upon the amount of hydrogen in solution in the steel. Thus, we have shown that after hydrogen treatment the same amount of hydrogen is evolved from a given steel during incubation, whether the specimen is aged at room temperature or heated to 150° C. immediately after quenching. It seems reasonable to assume that any change in the hydrogen content of the  $\alpha$ -iron will influence the hydrogen concentration in the retained austenite and so affect its stability.

Dr. Hoar's suggestion that the splitting of the first void might have a trigger action which would set off the neighbouring voids is interesting, but one which is extremely difficult to prove or disprove.

We agree with Mr. Parkin that there are many factors which influence the formation of hair-line cracks, but we believe that in the absence of hydrogen none of these other factors can by themselves produce internal defects of the type generally known as hair-line cracks.

In our opinion, the sudden evolution of hydrogen which occurs at the end of the incubation period indicates the beginning of trans-

formation of the retained austenite, but we doubt whether magnetic methods would be sufficiently sensitive to prove this, in view of the relatively small quantities of austenite involved.

As we stated in our reply to Mr. Pinder, we do not believe that hair-line cracks will be produced in a steel in the absence of a transformation, with its accompanying drop in hydrogen solubility. Other conditions being equal, the lower the temperature of the transformation the more easily is hydrogen retained, and, therefore, the greater the possibility of hair-line crack formation. It is, therefore, important to consider immunisation treatments in the light of the transformation characteristics of the steel.

We agree with the remarks on hydrides of iron but not with the statement that in solid steel the ratio of hydrogen to iron atoms is less than 1 in 2,000,000. This may be true when the steel is in equilibrium with hydrogen at atmospheric pressure and room temperature, but it is very easy to retain to room temperature a concentration of 1 : 3000 in solid steel by suitable cooling from high temperatures, as shown by our results with water-quenched hydrogen-treated specimens. Bearing in mind the existence of austenite, which implies local segregation of hydrogen, the effective concentration may be much greater than is represented by this figure.

We thank Mr. Parkin for the many suggestions which he has made. Some of them are impracticable, but we are hoping in the near future to carry out experiments on steels which are austenitic at room temperature, and to transform them by low-temperature treatment along the lines suggested by Mr. Parkin.

# AN INGOT OF RIMMED STEEL MADE BY THE BASIC OPEN-HEARTH PROCESS.<sup>1</sup>

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(Figs. 1 to 16 = Plates XVII. to XXIV.)

*Paper No. 13/1942 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

The manufacture and detailed examination of a rimmed-steel ingot are recorded. The examination included sulphur-printing of the longitudinal section of the ingot, chemical analysis throughout this section, and also micrographs of the zones which are particularly rich in sulphur.

Attention was particularly directed to the relationship of the carbon content of the core to the pit carbon value. In the ingot submitted the general analysis of the carbon in the core was lower than the pit analysis.

A survey of the rimmed-steel ingots published by the Committee on the Heterogeneity of Steel Ingots showed that the general analysis of the carbon in the core may be lower or higher than the recorded pit carbon content. An explanation of this phenomenon is derived from the balanced-composition hypothesis of Hultgren and Phragmén, which hypothesis has been developed mathematically to include the influence of manganese and pressure on the carbon and oxygen values of the balanced composition, and shows that with increasing manganese content as well as with increasing pressure the carbon content of the balanced composition is progressively increased.

The importance of ensuring that a pit sample is fully representative of the ladle analysis is stressed.

## STEELMAKING AND TEEMING DATA.

THE ingot selected was taken from the middle of a cast of rimming steel made by the open-hearth process. It was allowed to freeze without any addition of a stabiliser such as aluminium, or any other corrective, in order that the process of rimming could be studied in a simple form.

The following particulars give the working of the heat :

### *Bath samples.*

No.	Time, P.M.	Carbon. %.	Sulphur. %.	Phosphorus. %.	Manganese. %.
1	12.36	0.39	0.063	0.306	0.28
2	1.21	0.245	0.058	0.128	0.26
3	2.01	0.16	0.044	0.029	0.18
4	2.18	0.08	0.040	0.012	0.11
5	2.40	0.05	...	...	0.10

<sup>1</sup> Received September 2, 1942. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.



*Slag samples, corresponding to the above bath samples.*

No.	SiO <sub>2</sub> . %.	Al <sub>2</sub> O <sub>3</sub> . %.	CaO. %.	MgO. %.	S. %.	MnO. %.	P <sub>2</sub> O <sub>5</sub> . %.	FeO. %.	Fe <sub>2</sub> O <sub>3</sub> . %.	Total Fe. %.
1	16.6	2.0	52.8	5.04	0.18	5.40	12.20	2.04	3.60	4.10
2	11.4	2.0	51.9	4.60	0.24	4.60	12.60	8.77	3.79	9.50
3	10.4	1.8	51.1	4.53	0.27	4.80	12.40	8.80	5.72	10.80
4	9.2	1.5	47.0	4.10	0.29	4.40	9.52	16.89	6.86	18.00
5	9.2	1.5	46.8	4.10	0.29	4.38	9.32	14.70	9.30	18.00
Tapping	8.8	1.4	46.3	4.00	0.30	4.34	9.00	14.70	10.86	19.10

*Additions.*

*To Bath:* Between samples 1 and 2, 45 cwt. of scale.

Between samples 3 and 4, 5 cwt. of ore, 30 cwt. of scale.

*To Ladle:* 8 cwt. of ferro-manganese.

*Tapping time, 2.54 P.M.*

*Commenced teeming, 3.09 P.M.* Teemed through  $1\frac{1}{8}$ -in. nozzles into twenty-six 3-ton ordinary moulds, top-cast. Ingot 15 was selected for examination. Rimming commenced after 15 sec. and the ingot was capped after 18 min. The ingot rose  $2\frac{1}{2}$  in. in the mould, and was 5 ft. 8 in. high,  $20\frac{1}{2}$  in. square at the top and  $22\frac{1}{2}$  in. square at the bottom.

*Pit analysis.*

Carbon.	Sulphur.	Phosphorus.	Manganese.
0.08%	0.041%	...	0.30%
0.08%	0.042%	0.018%	0.29%

The bath samples analysed were killed in the sample pot with aluminium chips. An additional set of bath samples was drawn concurrently with the above killed samples Nos. 1 to 5, but these additional samples were allowed to freeze undisturbed—that is, without any aluminium addition. These unkilld bath samples were sectioned and polished (Fig. 1), and sulphur-printed (Fig. 2).

Micrographs of four of the slags, Nos. 1, 2, 3 and 6, taken with reflected light, are shown in Fig. 3. These micrographs show the change in constitution of the slags on passing from the melting to the finishing condition.

#### THE SECTIONING AND EXAMINATION OF THE INGOT.

The ingot was sectioned, planed and polished, to expose its vertical axis. Photographs of the polished surface and of the sulphur print are shown in Figs. 4 and 5.

The ingot was drilled in the standard positions,<sup>1</sup> and the drillings were analysed, with the following results:

Position.	Carbon. %.	Silicon. %.	Sulphur. %.	Phosphorus. %.	Manganese.
A	0.040	0.009	0.032	0.011	0.27
B	0.035	0.009	0.039	0.013	0.26
C	0.030	0.005	0.050	0.014	0.26
D	0.040	0.005	0.063	0.022	0.27
E	0.070	0.009	0.238	0.055	0.29
F	0.040	0.009	0.054	0.019	0.28
G	0.050	0.005	0.071	0.025	0.26
H	0.060	0.009	0.148	0.031	0.29

<sup>1</sup> See Fig. 2, p. 25, of the Fifth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1933, *Special Report No. 4*.

TABLE I.—*Analyses at Horizontal Layers in the Ingot.*

Mark.	Carbon. %.	Sulphur. %.	Phosphorus. %.	Manganese. %.
A1	0.050	0.028	0.012	0.27
2	0.055	0.028	0.010	0.28
3	0.050	0.028	0.010	0.27
4	0.050	0.028	0.011	0.27
5	0.040	0.025	0.012	0.28
6	0.030	0.023	0.011	0.28
7	0.035	0.024	0.010	0.28
8	0.040	0.024	0.011	0.26
9	0.040	0.027	0.011	0.28
10	0.040	0.026	0.012	0.26
11	0.040	0.026	0.012	0.28
B1	0.040	0.023	0.008	0.25
2	0.040	0.025	0.010	0.25
3	0.040	0.025	0.011	0.24
4	0.050	0.028	0.009	0.25
5	0.040	0.035	0.009	0.26
6	0.040	0.042	0.012	0.26
7	0.040	0.039	0.012	0.26
8	0.030	0.037	0.013	0.25
9	0.040	0.039	0.011	0.25
10	0.035	0.038	0.014	0.26
11	0.030	0.039	0.013	0.26
C1	0.040	0.027	0.010	0.27
2	0.040	0.027	0.009	0.27
3	0.035	0.028	0.009	0.25
4	0.040	0.027	0.009	0.24
5	0.045	0.033	0.013	0.25
6	0.035	0.041	0.013	0.26
7	0.040	0.045	0.016	0.25
8	0.045	0.057	0.019	0.26
9	0.040	0.050	0.018	0.24
10	0.035	0.044	0.015	0.25
11	0.035	0.044	0.016	0.25
D1	0.040	0.035	0.010	0.27
2	0.040	0.025	0.007	0.27
3	0.030	0.025	0.012	0.26
4	0.030	0.027	0.012	0.26
5	0.030	0.033	0.010	0.25
6	0.035	0.057	0.018	0.26
7	0.035	0.055	0.017	0.25
8	0.030	0.057	0.018	0.27
9	0.030	0.050	0.018	0.26
10	0.035	0.050	0.015	0.26
11	0.030	0.050	0.014	0.26
E1	0.030	0.032	0.013	0.28
2	0.030	0.025	0.018	0.27
3	0.030	0.025	0.011	0.28
4	0.030	0.028	0.015	0.26
5	0.030	0.057	0.017	0.26
6	0.040	0.045	0.016	0.27

TABLE I.—*Continued.*

Mark.	Carbon. %.	Sulphur. %.	Phosphorus. %.	Manganese. %.
<i>E7</i>	0.040	0.054	0.018	0.28
8	0.035	0.050	0.015	0.27
9	0.030	0.055	0.013	0.28
10	0.035	0.056	0.013	0.25
11	0.035	0.050	0.014	0.26
<i>F1</i>	0.035	0.030	0.011	0.26
2	0.035	0.028	0.012	0.26
3	0.025	0.028	0.013	0.25
4	0.020	0.027	0.011	0.24
5	0.015	0.091	0.027	0.27
6	0.035	0.066	0.028	0.25
7	0.030	0.071	0.023	0.27
8	0.030	0.066	0.022	0.27
9	0.030	0.067	0.022	0.25
10	0.030	0.064	0.021	0.26
11	0.025	0.064	0.020	0.27
<i>G1</i>	0.025	0.025	0.011	0.27
2	0.030	0.025	0.010	0.27
3	0.035	0.032	0.011	0.26
4	0.025	0.030	0.016	0.26
5	0.040	0.084	0.027	0.27
6	0.050	0.071	0.025	0.26
7	0.045	0.065	0.024	0.27
8	0.035	0.065	0.023	0.25
9	0.035	0.066	0.025	0.27
10	0.040	0.065	0.022	0.26
11	0.040	0.063	0.022	0.27
<i>H1</i>	0.026	0.030	0.014	0.29
2	0.034	0.025	0.012	0.26
3	0.030	0.029	0.011	0.26
4	0.024	0.028	0.011	0.26
5	0.042	0.079	0.028	0.30
6	0.044	0.080	0.027	0.27
7	0.040	0.075	0.025	0.27
8	0.036	0.069	0.026	0.29
9	0.044	0.067	0.026	0.28
10	0.050	0.064	0.026	0.29
11	0.043	0.065	0.028	0.27
<i>J1</i>	0.044	0.029	0.012	0.30
2	0.032	0.022	0.010	0.28
3	0.028	0.023	0.010	0.28
4	0.030	0.028	0.013	0.26
5	0.054	0.075	0.027	0.29
6	0.060	0.074	0.027	0.30
7	0.044	0.070	0.026	0.28
8	0.038	0.067	0.026	0.28
9	0.060	0.083	0.026	0.26
10	0.076	0.073	0.025	0.28
11	0.066	0.074	0.025	0.27

TABLE I.—*Continued.*

Mark.	Carbon. %.	Sulphur. %.	Phosphorus. %.	Manganese. %.
K1	0.040	0.035	0.012	0.29
2	0.030	0.024	0.014	0.28
3	0.030	0.024	0.012	0.27
4	0.030	0.028	0.012	0.26
5	0.036	0.055	0.016	0.31
6	0.048	0.083	0.026	0.29
7	0.042	0.079	0.027	0.29
8	0.040	0.077	0.028	0.27
9	0.064	0.077	0.029	0.29
10	0.050	0.090	0.029	0.31
11	0.060	0.148	0.031	0.29
L1	0.028	0.027	0.010	0.28
2	0.026	0.021	0.010	0.25
3	0.026	0.025	0.010	0.25
4	0.020	0.029	0.013	0.24
5	0.054	0.086	0.029	0.31
6	0.056	0.130	0.031	0.30
7	0.056	0.121	0.035	0.30
8	0.054	0.143	0.035	0.30
9	0.070	0.229	0.053	0.27
10	0.070	0.223	0.053	0.29
11	0.070	0.238	0.055	0.29
M1	0.030	0.030	0.013	0.26
2	0.028	0.025	0.010	0.24
3	0.026	0.025	0.010	0.26
4	0.030	0.026	0.013	0.26
5	0.022	0.028	0.012	0.27
6	0.024	0.029	0.011	0.26
7	0.022	0.035	0.014	0.27
8	0.022	0.035	0.014	0.26
9	0.040	0.059	0.022	0.28
10	0.030	0.066	0.022	0.29
11	0.060	0.123	0.031	0.43
11a	0.034	0.086	0.028	0.33
11b	0.044	0.090	0.030	0.35
11c	0.052	0.103	0.033	0.42

An analytical survey was made throughout the sectioned face of the ingot. Eleven equidistant points were marked at the bottom of the ingot from just under the skin to the centre. This was repeated throughout the length of the ingot at horizontal positions 6 in. apart. The analyses of these horizontal layers are shown in Table I., from  $A_1$  to  $A_{11}$  at the bottom of the ingot from skin to centre, to  $M_1$  to  $M_{11}$  at the top of the ingot from skin to centre. The actual positions of the drill holes are shown in Fig. 5.

Drillings at position  $M_{11}$  were found to have been contaminated with ingot scum rich in manganese.  $M_{11a}$ ,  $M_{11b}$  and  $M_{11c}$  were taken from the vicinity of position  $M_{11}$ .



This ingot scum which had collected in cavities immediately above position *E* (see Fig. 6) analysed :

FeO. %.	Fe <sub>2</sub> O <sub>3</sub> . %.	MnO. %.	SiO <sub>2</sub> . %.	CaO. %.	P. %.
30.3	6.0	57.3	2.9	Nil.	0.05

It may be remarked that this manganese-rich scum was in contact with metal in which the manganese content was even lower than that of the pit sample. The inference was that the manganese-rich scum was in equilibrium with a metal low in manganese. A heavy segregate near position *E* contained :

Sulphur . . . . .	0.514%
Manganese . . . . .	0.27%

#### EXAMINATION OF SULPHIDES.

As can be seen by the analysis at a point near *E*, the sulphur had risen to a value of 0.514% without a corresponding increase in manganese; in actual fact the manganese had a slightly lower value at this point than at other positions.

The natural inference was that at this point the sulphur was present as a free iron sulphide or as a solid solution rich in iron sulphide. Accordingly, a section was taken from this area and examined microscopically.

The inclusions present existed as a broken network and globules of a pale-yellow colour usually associated with pure iron sulphide. Only a very small number of grey inclusions were present, and these were associated with, or situated within, a yellow matrix. The grey portion of the inclusion was very pale, having a reflecting power about equal to that of the yellow sulphide. There was a very sharp delineation between the pale-grey and the yellow sulphide, no intermediate coloration being found; it therefore appeared probable that this pale-grey sulphide was a limiting solid solution between the iron- and manganese-bearing sulphide and gave the first indication of manganese in the inclusion.

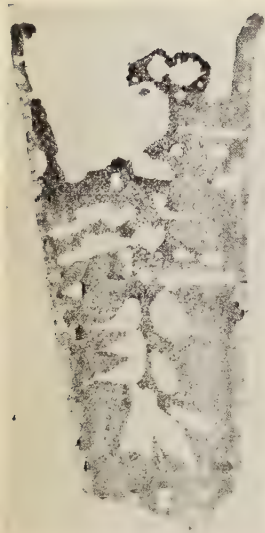
Figs. 7 and 8 show the arrangement and distribution of the yellow sulphide. Fig. 9 illustrates four yellow inclusions at the top, two showing traces of grey at the periphery; duplex inclusions in pale grey and yellow are at the bottom and one pale-grey inclusion on the left. At the top left of Fig. 10 is a large yellow sulphide inclusion with cleavages and a dotted area of pale grey. The inclusion at the right centre consists of a pale-yellow matrix with a dark-grey "greasy" portion, which appeared to be a silicate; the other inclusions are yellow with a small content of dark-grey sulphide. Figs. 7 to 10 were taken from the same section—*E*—and it should be noted that all the inclusions contain yellow sulphide.

The question as to the possible limits of the yellow sulphide now presented itself, and in order to settle this point a longitudinal piece



FIG. 1.—Split and Polished Unkilld Bath Samples.

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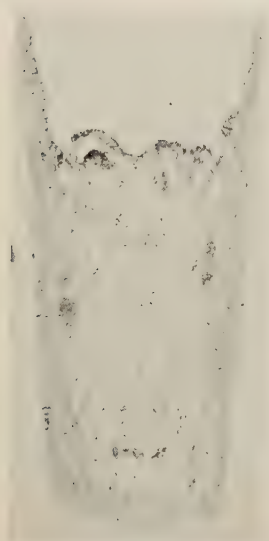
(a) No. 1.



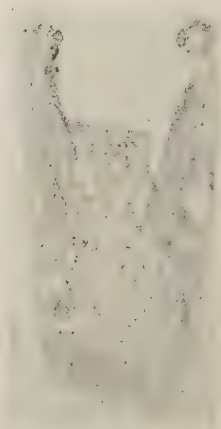
(b) No. 2.



(c) No. 3.



(d) No. 4.

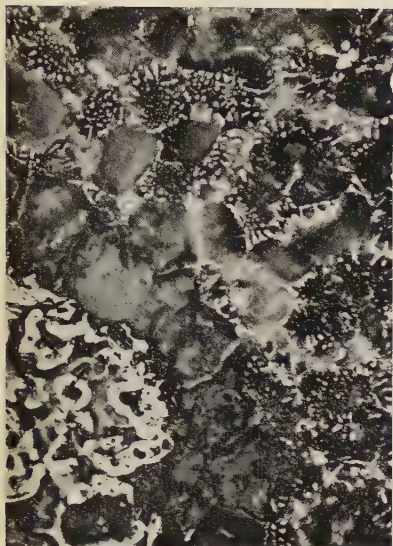


(e) No. 5.

FIG. 2.—Sulphur Prints of Bath Samples.

[Binnie.]





(a) No. 1.



(b) No. 2.



(c) No. 3.



(d) No. 6.

FIG. 3.—Steel Furnace Slags (reflected light).  $\times 100$  (reduced to four-fifths linear in reproduction).

[Binnie.



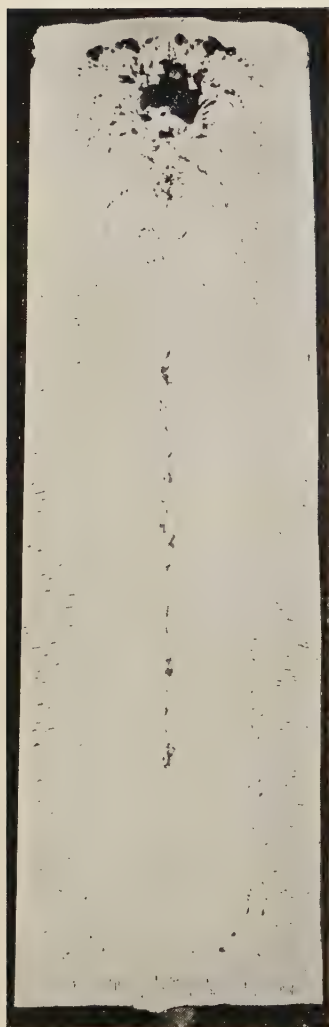


FIG. 4.—Polished Surface of the Ingot Section.

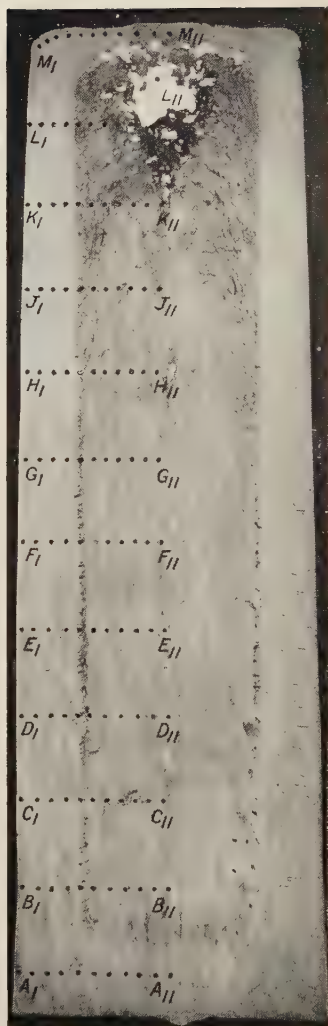


FIG. 5.—Sulphur Print of the Ingot Section, showing positions of drill holes.

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FIG. 6.—Sulphur Print in Region of Pipe.  $\times 1$  (reduced to three-fifths linear in reproduction).

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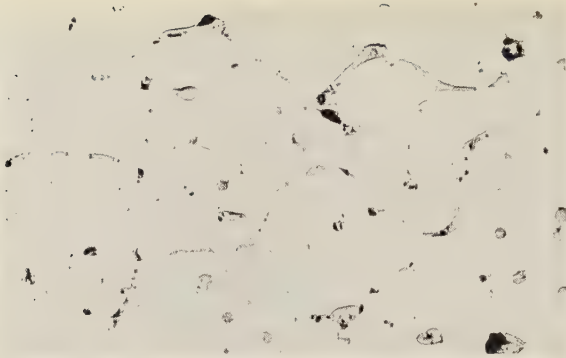


FIG. 7.—Arrangement and Distribution of Yellow Sulphide.  $\times 100$ .



FIG. 8.—Yellow Sulphide from same Micro-Specimen as Fig. 7.  $\times 100$ .

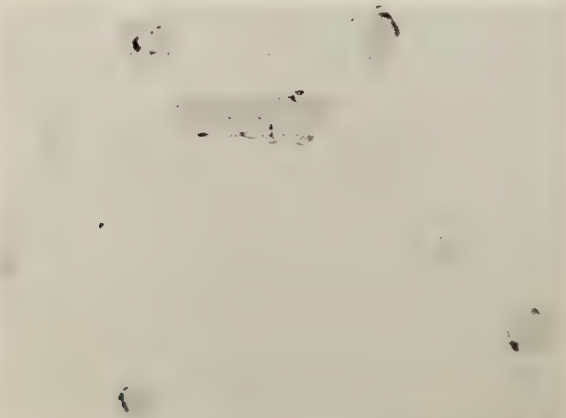


FIG. 9.—Distribution of Mixed Sulphide Inclusions.  $\times 250$ .

FIGS. 7 TO 9.—Sulphide Inclusions.

(Micrographs reduced to four-fifths linear in reproduction.)

[Binnie.]



FIG. 10.—Yellow Sulphide Inclusion, showing cleavages.  $\times 250$ .

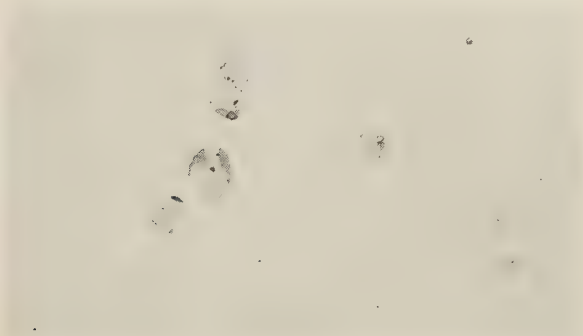


FIG. 11.—Pale- and Dark-Grey Inclusions in Yellow Matrix.  $\times 250$ .

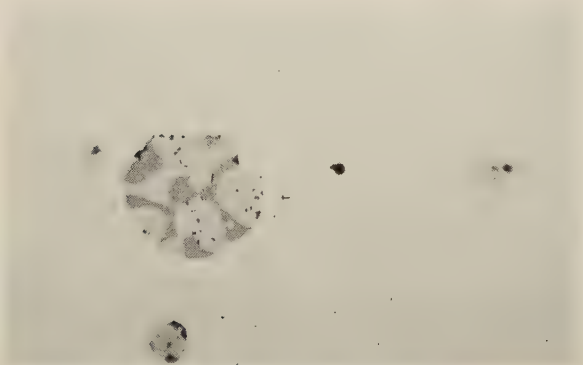


FIG. 12.—Medium-Grey Sulphide in Yellow Matrix.  $\times 250$ .

FIGS. 10 to 12.—Sulphide Inclusions.

(Micrographs reduced to four-fifths linear in reproduction.)

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FIG. 13.—Sulphur Print of Transverse Section from Pipe to Rim.

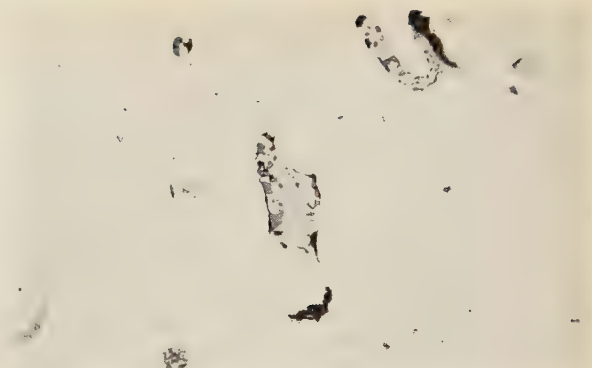


FIG. 14.—Pale- and Medium-Grey Inclusions in Yellow Matrix.  $\times 250$ .

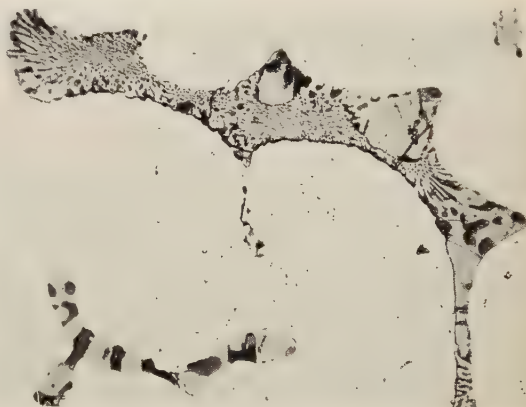


FIG. 15.—Eutectic Structure.  $\times 250$ .



FIG. 16.—Radiate Structure of Sulphides.  $\times 250$ .

FIGS. 14 to 16.—Sulphide Inclusions.

(Micrographs reduced to four-fifths linear in reproduction.)

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was cut from the ingot to include the positions *E* and *H*. This was sulphur-printed and sections were prepared from an 8-in. strip cut from the centre downwards. The sulphur print is shown in Fig. 6 and the structure of the sulphides in Figs. 11 and 12.

The top inclusion in Fig. 11 had a pale-grey globule and a dark-grey corner embedded in a yellow matrix, the two left-centre and one right-centre inclusions consisted of medium- and dark-grey material, whilst those at the lower right were yellow. The large inclusion in Fig. 12 consisted of pale- and medium-grey material, as did the one almost immediately below, whilst three yellow inclusions were seen in close proximity.

In all the sections taken from the strip including positions *E* and *H* there were present homogeneous yellow, duplex in yellow and pale grey, duplex in pale and medium grey, and medium-grey homogeneous sulphide inclusions.

Another strip was taken from the ingot, this time in a transverse direction from approximately the point *E* to the rim. The sulphur print is shown in Fig. 13.

Figs. 14, 15 and 16 show typical structures of the sulphides. Homogeneous yellow sulphides in varying quantity were present in all sections up to the rim and in association with duplex in yellow and pale grey, duplex in medium and pale grey, and inclusions in which pale and medium grey were embedded in a yellow matrix. Such an inclusion is seen in the centre of Fig. 14.

Fig. 15 shows a eutectic structure found midway between position *E* and the rim; the matrix was yellow, the second constituent was medium grey and the globules at the middle of the right-hand limb were of a darker grey. The inclusion in the lower left corner consisted of dark-grey globules in a yellow matrix. Fig. 16 illustrates the radiating structure of the sulphides on approaching the rim zone.

In a very narrow transition zone between the core and rim the number of inclusions decreased rapidly, with a quick change from duplex in pale and medium grey to a homogeneous medium grey. As would be expected, only a very small amount of sulphide was present in the rim and was of a medium-grey colour.

#### THE CORE OF THE INGOT.

The general analysis of the core of the ingot showed a loss in carbon from the pit figure of 0.08%. Also, in the lower half of the ingot the carbon in the core was rather less than that in the rim. The highest carbon percentage, 0.07–0.076%, was found to lie along the axis at the upper portion of the core, and even this figure did not exceed the pit carbon figure :

Pit carbon . . . . .	. 0.08%
Average core carbon . . . . .	. 0.045%
Average rim carbon . . . . .	. 0.03%

The carbon in the rim was, as is usually found, higher in the lower portion of the ingot than in the upper regions.

Sulphur and phosphorus had segregated in line with each other, but, as usual, the degree of segregation of the sulphur was greater than that of the phosphorus.

The segregation of manganese was confined to a range which extended at the upper limit to about the pit figure. No figure for manganese content sensibly exceeded the pit figure of 0.29-0.30%.

Hultgren and Phragmén<sup>1</sup> stated that, for liquid steel with higher carbon than the balanced composition, the carbon would increase in the liquid metal during freezing under gas evolution; for metal of lower carbon content than the balanced composition the opposite held, i.e., the carbon in the liquid metal during freezing would decrease. They fixed the carbon content of the balanced composition at about 0.06%.

An explanation of balanced composition is also to be found in a review by C. A. Edwards<sup>2</sup> on the original paper by Hultgren and Phragmén. T. Swinden, in the same Report,<sup>3</sup> also discussed the balanced composition.

The  $\delta$  liquidus zone of the iron-carbon-oxygen diagram, for carbon and oxygen percentages associated with rimming steel, is a dilute solution; the depression of the freezing point for such percentages is linear and additive.

Papers discussing the  $\delta$  liquidus zone of the iron-carbon-oxygen diagram assume the surface to be plane, an assumption which, at any rate for the carbon and oxygen percentages of rimming steel, must be very nearly true.

The equation of this plane which passes through the  $x$  carbon co-ordinate at 0.51% carbon and 1492° C., the  $y$  oxygen co-ordinate at 0.24% oxygen and 1520° C., and the  $z$  temperature co-ordinate at 1537° C., is:

$$\frac{x}{0.51} + \frac{y}{0.24\left(\frac{45}{17}\right)} + \frac{z}{45} = 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

using the iron-carbon peritectic temperature of 1492° C. as the datum line.

The carbon-oxygen product, 0.0025, or, more generally, 0.0025A, where A represents the pressure in atmospheres, gives a surface:

$$xy = 0.0025 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

<sup>1</sup> *Jernkontorets Annaler*, 1938, vol. 122, No. 8, p. 377.

<sup>2</sup> Ninth Report on the Heterogeneity of Steel Ingots, Section II., *Iron and Steel Institute*, 1939, *Special Report* No. 27.

<sup>3</sup> Ninth Report, Section III., *loc. cit.*

eliminating  $y$ , say :

$$z = 45 - \frac{45x}{0.51} - \frac{17(0.0025)}{0.24x} \quad \dots \quad (3)$$

$$\frac{dz}{dx} = -\frac{45}{0.51} + \frac{17(0.0025)}{0.24x^2}$$

$$\text{for } x_{\max.} \quad \frac{17(0.0025)}{0.24x^2} = \frac{45}{0.51}$$

whence  $x$ , the carbon percentage at the balanced composition = 0.045%,  
and  $y$ , the oxygen percentage at the balanced composition = 0.056%.

A table of balanced compositions for various pressures can be constructed, as shown in Table IIA.

If the steel contained manganese, Hultgren and Phragmén stated, the only appreciable modification of the iron-carbon-oxygen ternary diagram was that the oxygen solubility surface moved towards lower oxygen content. For 0.30% of manganese the point  $B$  in Fig. 2 of their paper was displaced from 0.24% to 0.12% of oxygen. Using this value in a fresh calculation the balanced compositions became those shown in Table IIB.

TABLE II.—*Balanced Compositions.*

	A. Manganese nil.			B. Manganese 0.30%.		C. Manganese 0.55%.		
Pressure. Atm.:	1.	2.	4.	1.	2.	1.	1½.	2.
Carbon. % . . .	0.045	0.063	0.090	0.063	0.090	0.080	0.098	0.110
Oxygen. % . . .	0.056	0.070	0.110	0.040	0.056	0.031	0.036	0.045
Depression of freezing point. ° C. .	7.9	11.1	15.8	...	...	...	...	...

Putting equations (1), (2) and (3) into a general form, where :

$A$  = pressure in atmospheres,

$B$  = the monotectic point, which becomes a eutectic point when the manganese exceeds 0.34%, from the iron-oxygen diagram,

$s$  = carbon-oxygen product in weight percentage, assumed in the present discussion to be 0.0025,

then, within certain limits :

$$x, \text{ the carbon percentage at the balanced composition} = 0.44 \sqrt{\frac{As}{B}}$$

$$y, \text{ the oxygen percentage at the balanced composition} = \frac{\sqrt{AsB}}{0.44}$$

Carrying the argument a little further and using a manganese content of 0.55%, the point  $B$  occurs at 0.075% oxygen, whence the balanced compositions became those recorded in Table IIC.



The calculated carbon and oxygen percentages at the balanced compositions show the upward trend of the carbon at that composition for increasing manganese contents.

#### EXAMINATION OF RIMMED-STEEL INGOTS FROM THE POINT OF VIEW OF BALANCED COMPOSITION.

When the carbon percentage was above that of the balanced composition the composition of the liquid portion of the freezing ingot changed towards higher carbon and lower oxygen contents, and *vice versa*. Owing to circulation and the freezing of the core metal, which behaved as if it were an ingot inside an ingot, the average carbon analysis throughout the whole core should be higher than the carbon of the pit sample when the pit carbon was above the balanced composition, and should be lower than the carbon of the pit sample when the pit carbon was below the balanced composition. Of course the argument assumed that the gas reaction :



occurred entirely or almost entirely at the liquid-solid face of the advancing wall. The greatest evolution of gas occurred at and near the balanced composition, and, for carbon contents well below the balanced composition, the phenomenon was apt to be masked by less simple laws of freezing; for example, with carbon contents much lower than the balanced composition the monotectic line would be reached when the carbon, after an initial decrease, would commence to increase.

#### EXAMINATION OF PUBLISHED DETAILS OF INGOTS.

In the present example, with a pit carbon value of 0.08% and manganese 0.30%, the average analysis of the core, say, 0.045% of carbon, was well below the pit carbon. For ingot No. 61 of the Ingot Committee,<sup>1</sup> with a pit analysis of 0.08% of carbon and 0.38% of manganese, a few figures for core analysis were recorded which suggested that the core carbon in this instance also was below the pit carbon, but not to the same extent as in the present ingot. Nead and Washburn,<sup>2</sup> with a pit carbon of 0.097% and manganese about 0.40%, reported an average core analysis of 0.064% of carbon.

These pit analyses, according to the balanced composition, Table IIb., were just below the balanced composition and incidentally in the zone of maximum gas evolution, provided that a pressure of 1.5–2 atm. was considered for the pressure to be associated with the gas reaction.

<sup>1</sup> Fifth Report, *loc. cit.*, p. 30.

<sup>2</sup> *Metals and Alloys*, 1934, vol. 5, p. 43.

Swinden's ingot <sup>1</sup> had a pit analysis of carbon 0.10% and manganese 0.32%, and even with a reaction pressure of 2 atm. the analysis, according to Table IIB., was still above the balanced composition. His analysis (*loc. cit.*, p. 27) suggested that if the entire core had been sampled the core analysis would have been above the pit carbon figure.

Ingot No. 65,<sup>2</sup> with a pit analysis of 0.05% of carbon and 0.05% of manganese, from the balanced composition, Table IIA., and for a gas reaction pressure a little above atmospheric, was below the balanced composition. The core analysis (*loc. cit.*, p. 23) suggested that a full core analysis would have been below the pit carbon, or at any rate the carbon would not have been higher than the pit carbon. This ingot might have been on the balanced composition.

Ingot No. 62,<sup>3</sup> with a pit analysis of 0.02% of carbon and 0.028% of manganese, showed a general ingot analysis every point of which was higher than the pit carbon. Even at position *A* the carbon was 0.039%. The inference is that the pit carbon recorded was low. Much the same remarks could apply to ingot No. 59<sup>4</sup> and to ingot No. 24.<sup>5</sup>

Of ingots Nos. 63 and 64,<sup>6</sup> teemed from the same heat, No. 64 was examined in detail by Swinden.<sup>7</sup> Its pit analysis was carbon 0.06% and manganese 0.54%, which placed it considerably lower than the balanced composition. Both ingots, No. 63 as well as No. 64, showed only slight ebullition and gave signs of freezing when the mould was only half full. The balanced composition came out at at least 0.08% of carbon, possibly nearer 0.09% or 0.10%, and for 0.54% of manganese the eutectic point *B* had been displaced towards lower oxygen and higher carbon contents to such an extent that oxygen could have been thrown out as complex oxide, FeO-MnO, concurrently with the removal of oxygen by any gas ebullition reaction. If early freezing increased the gas reaction pressure in the ingot the removal of oxygen as an FeO-MnO complex became understood.

The rimmed-steel ingots described in the Reports of the Ingot Committee would appear to support the balanced-composition hypothesis enunciated by Hultgren and Phragmén. To establish a complete experimental verification of the hypothesis the carbon content and also the oxygen content of the liquid metal in the ladle would require to be known accurately.

<sup>1</sup> Cast 34/8940, Ninth Report on the Heterogeneity of Steel Ingots, *loc. cit.*, p. 23.

<sup>2</sup> Sixth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1935, *Special Report* No. 9, p. 24.

<sup>3</sup> Fifth Report, *loc. cit.*, p. 38.

<sup>4</sup> Fourth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1932, *Special Report* No. 2.

<sup>5</sup> Second Report on the Heterogeneity of Steel Ingots, *Journal of the Iron and Steel Institute*, 1928, No. I., p. 480.

<sup>6</sup> Sixth Report, *loc. cit.*, Section II.

<sup>7</sup> Seventh Report, *loc. cit.*, Section II.; Ninth Report, *loc. cit.*, Section III.

In the published examinations of rimmed-steel ingots the pit carbon analysis recorded was, in many instances, obviously too low, and investigators of rimming-steel ingots should, in future, pay particular attention to this point.

The author wishes to record his thanks to the directors of The Lancashire Steel Corporation, Ltd., for permission to publish this paper, and also to the staff of the laboratories for the analyses, sulphur-printing and photographic work recorded.

[This paper was discussed jointly with the following two by J. Mitchell on "Rimming Steel," and two by T. Swinden on "Rimming Steel," and by T. Swinden and W. W. Stevenson on "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C."]

## RIMMING STEEL.<sup>1</sup>

### COMPARATIVE STUDY OF THREE INGOTS RECEIVED FROM SOC. ANON. DES HAUTS FOURNEAUX, FORGES ET ACIÉRIES DE DENAIN ET D'ANZIN, AT DENAIN, FRANCE.

PRESENTED ON BEHALF OF THE COMMITTEE ON THE HETEROGENEITY OF STEEL INGOTS BY

J. MITCHELL (MESSRS. STEWARTS AND LLOYDS, LTD.).

(Figs. 1 to 3 = Plates XXV. to XXVII.)

*Paper No. 12/1942 of the Committee on the Heterogeneity of Steel Ingots.*

#### SUMMARY.

The analytical results obtained on two low-carbon basic Bessemer steel ingots are tabulated and compared with similar results obtained on earlier samples reported upon by the Committee on the Heterogeneity of Steel Ingots. The figures include variations in analysis found in the rim and core, and these are discussed from the standpoint of the light which they throw on the practical aspect of the rimming process.

#### INTRODUCTION.

IN 1934, through the courtesy of Monsieur F. Clerf, two ingots of basic Bessemer steel were submitted for examination to the Committee on the Heterogeneity of Steel Ingots. Arising out of the Committee's report on these ingots<sup>2</sup> and the discussions which it provoked, it was resolved to secure further ingots from the same source, and the Committee have again to acknowledge their gratitude to Monsieur Clerf for his assistance in providing two further ingots. These ingots were made in 1939, again under the personal observation of Mr. A. G. Hock and Mr. R. H. Myers, and, when the full analytical data became available, it was felt that the most useful way of presenting these was to include with them a comparative study of all the ingots received from Denain.

The Committee considered that the ingots provided an exhibit of a gradually changing character, which probably represented the whole range of probable structures encountered in ordinary rimming practice with low-carbon basic Bessemer steel.

<sup>1</sup> Received July 2, 1942.

<sup>2</sup> Sixth Report on the Heterogeneity of Steel Ingots, pp. 19-23, *Iron and Steel Institute*, 1935, *Special Report No. 9*.



The following report considers, in some detail, three basic Bessemer rimmed steel ingots :

*Example 64* (Blow 2835) made at Denain in July, 1934, and already reported upon in the Sixth Report of the Heterogeneity of Steel Ingots Committee, and further examined and reported upon in the Seventh and Ninth Reports. As full analytical data are only available for ingot 64, and as it has already been noted (*loc. cit.*, p. 23) that there is little difference between the two ingots obtained at this time, it is proposed, for the purposes of the following report, to ignore ingot 63.

*Ingot No. 9368* (Blow 4971) made at Denain in July, 1939.

*Ingot No. 9369* (Blow 4943) made at Denain in July, 1939.

For convenience, these ingots will be referred to as 64, 9368 and 9369.

#### COMPARISON OF DATA.

The following data are available for these three ingots :

- (1) Particulars of steelmaking practice.
- (2) Sulphur prints and macro-etchings of centre sections.
- (3) Analyses of centre sections at the Committee's standard positions.
- (4) Detailed analyses, including oxygen and nitrogen determinations, of a strip at the middle of the length from the edge to the centre of each ingot.

##### (1) *Steelmaking Practice.*

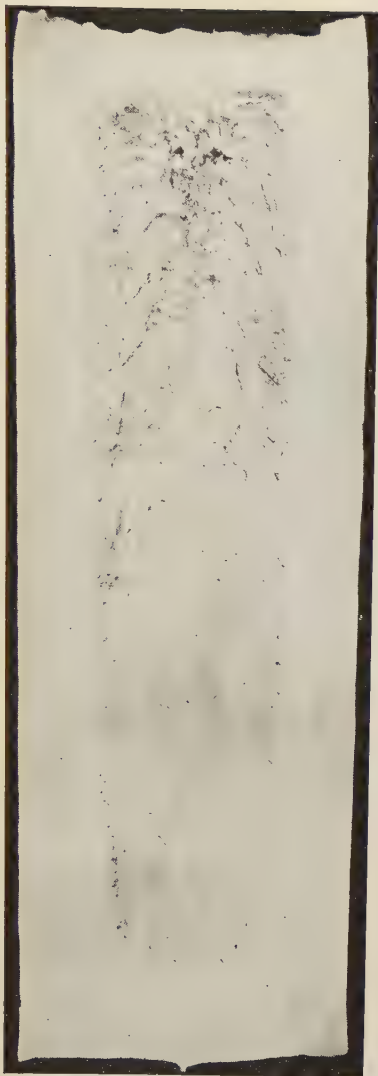
The details of each blow, together with metal and slag analyses, are given in Tables I., II. and III. for purposes of detailed record, and these are summarised for comparative purposes in Table IV.

##### (2) *Ingot Sections.*

As all three ingots were cast in similar moulds, comparison of the general characteristics of each can be made with the factor of mould size eliminated. The general ingot dimensions were 6 ft. 6 in. long, 1 ft. 10 in. square at the bottom, 2 ft. 1½ in. square at the top. These dimensions represent an ingot of approximately 4.5 tons weight. The ingots were cast big-end-up, and it is possible that an examination of similar ingots cast in narrow-end-up moulds might not present exactly the same features.

Reproduction of the sections after sulphur-printing and macro-etching are shown in Figs. 1, 2 and 3.

Considering first the general structure of the ingot sections, which were prepared by parting exactly on the centre line, considerable differences are revealed on sulphur-printing and macro-etching.



(a) Sulphur Print.

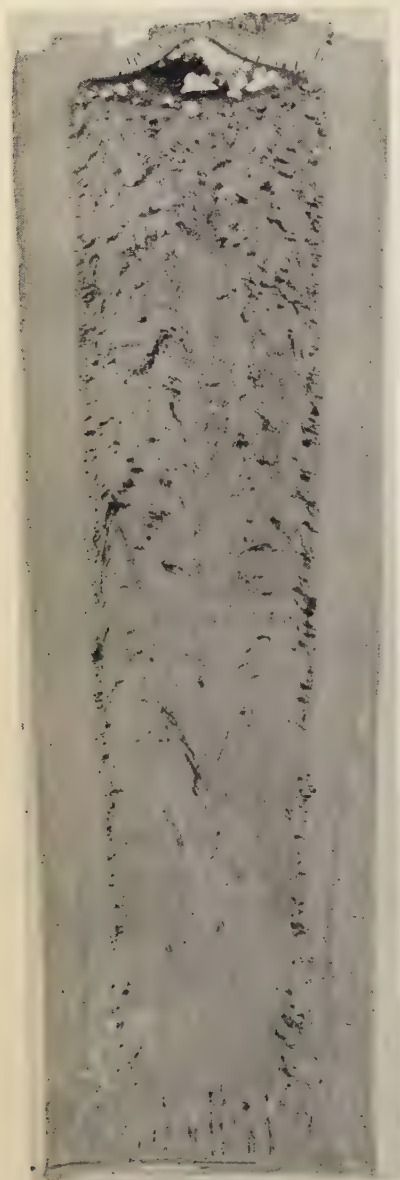


(b) Macro-etched Surface.

FIG. 1.—Ingot 64.

[*Mitchell*

[*To face p. 296 p.*



(a) Sulphur Print.



(b) Macro-etched Surface.

FIG. 2.—Ingot 9368 (Cast No. 4971).

[Mitchell.]



(a) Sulphur Print.



(b) Macro-etched Surface.

FIG. 3.—Ingot 9369 (Cast No. 4943).

[Mitchell.







TABLE II.—Details of Blow 4911 (Ingot No. 9308).

Time		Analyses.						
		C. %	Si. %	Mn. %	S. %	P. %	O. %	N. %
	Lime (including 300 kg. from previous blow)							
	Scrap (includes 50 kg. added later)							
	Mixed iron (before desulphurisation). Soda ash used (100 kg.)	3.71	0.270	0.929	0.089	1.68	0.005	0.006
	<i>Charge.</i>							H. ml. per 100 g.
								...
	Turned up							
	Turned down							
	Turned up							
	Turned down							
	Sample for judging phosphorus							
	Turned up	0.018	0.002	0.389	0.042	0.196	0.048	0.016
	Turned down							
	Sample for judging phosphorus							
	aluminium-killed	0.013	0.001	0.356	0.033	0.109	0.046	0.015
	Two samples { unskilled	0.016	0.001	0.352	0.033	0.114	0.030	0.014
	Scrap added	0.018	0.002	0.345	0.033	0.109	0.048	0.017
	Turned up							
	Turned down							
	Sample for judging phosphorus							
	Added Fe-Mn (80%)	0.011	0.001	0.263	0.034	0.065	0.056	0.016
	Stirred by slight movement of vesse							
	Started slagging							
	Slag sample : SiO <sub>2</sub> , 4.40%; Al <sub>2</sub> O <sub>3</sub> , 0.66%; FeO, 4.10%; MnO, 4.24%;							
	Fe <sub>2</sub> O <sub>3</sub> , 3.56%; CaO, 55.10%; MgO, 0.40%; P <sub>2</sub> O <sub>5</sub> , 27.05%; S (as							
	sulphide), 0.121%; SO <sub>2</sub> , 0.170%; alkali oxide, 0.091%.							
	Two samples { unskilled	0.040	0.001	0.494	0.033	0.071	0.041	0.016
	Lime for bridging	0.043	0.001	0.559	0.034	0.070	0.047	0.016
	Started pouring into ladle							
	Added Fe-Mn (80%) to ladle							
	<i>Casting Details.</i>							
	Opened out into 1st pair of moulds							
	Opened out into 2nd pair of moulds							
	Two pit samples { aluminium-killed	0.065	0.001	0.655	0.035	0.088	0.039	0.014
	Finished teeming 4th ingot, which was accepted for examination	0.051	0.001	0.658	0.032	0.082	0.042	0.016
	Sample of sheet bar taken from middle of 3rd ingot	0.059	0.001	0.708	0.036	0.087	0.026	0.014

*Rimming Details.*

Initial effervescence was slight and sluggish and, as is usual in such cases, was distributed generally rather than being confined to the freezing wall. Considerable slag and metal crust formed centrally almost immediately, but it could be seen that effervescence was becoming stronger at the freezing wall.

Dusted the crust of the 4th ingot with crushed anthracite to facilitate removal.

On removal of crust with stake, effervescence improved and became localised at 10.00 only a 2-in. square hole of exposed liquid remained in the centre. slag formed subsequently. Thereafter the ingot rimmed in normally until at 10.00 only a 2-in. square hole of exposed liquid remained in the centre.

Ingot blowing slightly through central vent, so put on small plate. It is important to note that the companion ingots of this blow, the tops of which were not disturbed, froze over completely 1½ min. after teeming each ingot, the tops showing a 2-in. to 3-in. rise and several peaks round the slag vents.

TABLE III.—Details of Blow 4943 (*Ingot No. 9369*).

						Analyses.							
						C. %.	Si. %.	Mn. %.	S. %.	P. %.	O. %.	N. %.	H., ml. per 100 g.
Charge													
Lime (includes 300 kg. from previous blow)	.	.	.	.	.								
Scrap	.	.	.	.	.								
Mixer iron (before desulphurisation)	.	.	.	.	.								
Soda ash used (50 kg.)	.	.	.	.	.	3.09	0.260	0.951	0.080	1.69	0.0045	0.0045	1.3
Blowing Details.													
Time													
11.35	Turned up												
11.51	Turned down												
11.55	Sample for judging phosphorus	.	.	.	.								
11.55½	Turned up												
11.55½	Turned down												
11.56	Sample for judging phosphorus	.	.	.	.	0.017	0.001	0.302	0.047	0.078	0.063	0.013	...
11.56	Two samples { aluminium-killed	.	.	.	.								
11.57	Added Fe-Mn (30%)	.	.	.	.	0.011	0.002	0.223	0.035	0.040	0.068	0.013	0.35
11.57	Turned up	.	.	.	.	0.019	0.002	0.242	0.035	0.043	0.044	0.012	0.25
11.57½	Started slagging	.	.	.	.	0.014	0.001	0.227	0.037	0.042	0.070	0.013	0.55
12.00	Finished slagging	.	.	.	.								
12.5	Sample for judging phosphorus	.	.	.	.								
12.5	Two samples { aluminium-killed	.	.	.	.								
12.9	Slag sample: SiO <sub>2</sub> , 4.72%; Al <sub>2</sub> O <sub>3</sub> , 0.64%; FeO, 7.29%; MnO, 5.00%; CaO, 55.20%; MgO, 0.34%; P <sub>2</sub> O <sub>5</sub> , 22.03%; S (as sulphide), 0.144%; SO <sub>2</sub> , 0.26%; alkali oxide, 0.08%.	.	.	.	.	0.031	0.002	0.279	0.033	0.040	0.054	0.012	...
12.9	Lime for bridging	.	.	.	.	0.024	0.002	0.273	0.034	0.041	0.062	0.012	0.10
12.13	Started pouring into ladle	.	.	.	.								
12.14	Added Fe-Mn (80%) to ladle	.	.	.	.								
Casting Details.													
12.19	Opened out into 1st mould												
12.21	Opened out into 2nd and 3rd moulds												
12.22½	Two pit samples { aluminium-killed	.	.	.	.	0.050	0.002	0.444	0.033	0.048	0.050	0.012	1.35
12.23	Finished teeming 3rd ingot, which was accepted for examination	.	.	.	.	0.047	0.002	0.445	0.035	0.046	0.057	0.011	0.20
	Sample of sheet bar taken from middle of 2nd ingot					0.047	0.002	0.440	0.036	0.049	0.035	0.014	0.20
Finishing Details.													
12.25	Efferesced freely during and on completion of teeming.												
12.26-38	Removed slag with stake. Little or no slag appeared to form subsequently.												
12.40	Rimmed-in progressively to the centre accompanied throughout by free effervescence at the freezing wall.												
12.40	Top solid, with the usual slight blowing through central vent. Ingot tops sank 1 in.												

*Running Details.*

Considerable slag started to form in centre of top almost immediately. Ingot tops sank 1 in.



TABLE IV.—*Steelmaking Data.*

Ingot No. :	64.	9368.	9369.
<i>Charge.</i>			
Mixer metal . . . . .	28,700 kg.	34,800 kg.	26,000 kg.
Scrap . . . . .	2,100 kg.	1,000 kg.	500 kg.
Percentage of total metallic charge .	6.8%	2.8%	1.9 %
Lime . . . . .	3,500 kg.	3,500 kg.	2,680 kg.
Including slag from previous heat .	200 kg.	300 kg.	300 kg.
<i>Mixer Metal Analysis.</i>			
Total carbon. % . . . . .	3.740	3.710	3.690
Phosphorus. % . . . . .	1.840	1.680	1.690
Sulphur. % . . . . .	0.047	0.089 *	0.080 *
Silicon. % . . . . .	0.340	0.270	0.260
Manganese. % . . . . .	1.460	0.930	0.950
Nitrogen. % . . . . .	0.0030	0.0060	0.0045
<i>Blown Metal before Manganese Addition.</i>			
Phosphorus. % . . . . .	0.039	0.065	0.040
Sulphur. % . . . . .	0.026	0.034	0.035
Silicon. % . . . . .	<0.005	0.001	0.002
Manganese. % . . . . .	0.250	0.263	0.223
Carbon. % . . . . .	0.030	0.011	0.011
Nitrogen. % . . . . .	0.016	0.017	0.015
Oxygen (unkilled samples) . . . . .	0.050 †	0.056	0.068
Ferro-manganese additions . . . . .	165 kg. (78% Mn) to ladle.	245 kg. (80% Mn) to vessel before slag-ging, 20 kg. (80% Mn) to ladle.	167 kg. (80% Mn) to vessel before slag-ging, 105 kg. (80% Mn) to ladle.
<i>Pit Sample.</i>			
Phosphorus. % . . . . .	0.048	0.082	0.046
Sulphur. % . . . . .	0.026	0.032	0.035
Silicon. % . . . . .	<0.005	0.001	0.002
Manganese. % . . . . .	0.540	0.650	0.450
Carbon. % . . . . .	0.060	0.051	0.047
Nitrogen. % . . . . .	0.016	0.017	0.015
Oxygen. % . . . . .	...	0.047	0.057
<i>Teeming Data.</i>			
Nozzle . . . . .	35 mm.	35 mm.	35 mm.
Casting temp. . . . .	1480° C.	1480° C.	1520° C.
Teeming time . . . . .	2 min. 30 sec.	2 min.	2 min.
Idle time during blow . . . . .	29 min.	23½ min.	22½ min.
<i>Finishing Slag.</i>			
SiO <sub>2</sub> . % . . . . .	5.10	4.40	4.72
CaO. % . . . . .	47.90	55.10	55.20
MgO. % . . . . .	2.10	0.40	0.34
MnO. % . . . . .	5.80	4.24	5.00
Al <sub>2</sub> O <sub>3</sub> . % . . . . .	0.80	0.66	0.64
FeO. % . . . . .	11.70	4.10	7.29
Fe <sub>2</sub> O <sub>3</sub> . % . . . . .	5.40	3.56	4.30
P <sub>2</sub> O <sub>5</sub> . % . . . . .	20.30	27.05	22.03

\* Before desulphurisation.

† Calculated from manganese loss.

The ratios of rim material to core material on any section other than one taken at the extreme top or bottom of the ingot are as follows :

Ingot No. . . . .	64	9368	9369
Area of rim to area of core . . . . .	2.06	1.46	1.30

The last two figures are within the limits usually experienced with basic Bessemer rimmed steel in the carbon range shown by

these samples, but the ratio for ingot 64 indicates a much greater quantity of rim material than is normal.

The sections at the top of each ingot call for special comment. Ingot 64 shows a top covered by a crust which appears to be almost as thick as the rim itself, but in ingots 9368 and 9369 the crust thins out towards the ingot centre in a manner to be expected from the normal sequence of events during rimming. It is probable that there was some considerable difference in the way in which the crusts of the two distinct types were formed.

The observers reported that the rimming action in ingot 64 was slightly obscured by a crust of metal and that there was no visible evolution of gas. The section conveys the impression that this crust must have grown continuously as the metal rose in the mould and that its formation might be due, in part at least, to solidification without any assistance from rimming action.

In the case of ingot 9368, it is reported that initial effervescence was small and sluggish; considerable slag and metal crust formed almost immediately, whilst for ingot 9369 only slag is reported on the ingot top with a free rimming action. The crusts in both 9368 and 9369 are very similar, although that in 9368 is the thicker of the two. These two tops differ also in general form; ingot 9368 is slightly arched while 9369 is concave, except at the last point to solidify.

The ingots present interesting differences as regards blow-hole distribution. There is very little indication of gas-holes in ingot 64, except at the lower part of the ingot, and even there the volume of entrapped gas does not appear to be very great. The number and size of the gas-holes at the junction of the rim and core are also relatively small.

Ingot 9368 shows the greatest gas separation in the rim material and also at the junction of the rim and core. The elongated gas-holes in the rim extend fully one-third of the ingot length, and both the size and number of the junction holes are much greater than in the other two cases. These observations confirm the observers' report that the rimming action which was slow in starting was accompanied by a rise in the metal.

Ingot 9369 shows a normal number of rim gas-holes extending approximately for one-quarter of the length of the ingot, but the thickness of metal between the outside surface and these holes is greater than in 9368. The distribution of the junction gas-holes is very uniform and they are of small size. The general effect of this arrangement is to create the appearance of a sharp line of demarcation between rim and core. Indeed, at the top part of this ingot there is a distinct suggestion that the core has been freezing inside a previously formed rim, as if the rim had, in fact, acted as an external mould during the last liquid stages of rimming.

The sulphur prints show the usual marked difference in structure between rim and core, and it should be noted that the hetero-

geneity of the lower part of 64 and 9369 is much less marked than in ingot 9368. The macro-etching also indicates the same difference in texture between 9368 and the other two sections.

Attention is drawn to the V-shaped segregated area at the top of 9369—an apparent irregularity which is absent in the other two cases. A further difference in this ingot, calling for remark, is the string of axial segregate extending almost the full length of the ingot from the bottom of the V-shaped segregate.

### (3) *Analyses at Standard Positions.*

The results of analyses at standard positions are shown in Figs. 4, 5 and 6.

It will be noted that the position from which analysis samples were taken in ingots 9368 and 9369 have been varied slightly from the usual practice of the Committee. This was done to indicate differences between the material in the rim, material at the junction of the rim and core and material at the axis of the ingot.

It is proposed here merely to discuss, in general terms, the distribution of the various elements and to reserve more detailed discussion of rim and core differences for the next section.

A comparison of the composition at various positions shows that, in all cases, there is a pronounced segregation of carbon, sulphur and phosphorus in the core as compared with the rim, and this remark applies, in lesser degree, to nitrogen, nickel and arsenic. There is, in addition, a segregated portion within the segregate in the upper part of each ingot.

In Tables V. and VI. an attempt is made to indicate the degree of segregation in the top portion of the ingot and throughout the middle of its length by relating the percentages of the various elements present to the pit analyses. Bearing in mind that the greater the departure from unity in the figure given in these Tables, the greater is the degree of segregation, some interesting comparisons may be drawn between the three ingots under consideration.

TABLE V.—*Degree of Segregation at Top of Ingots based on Analyses at Standard Positions.*

Position : Ingot No. :	E. 64.		E, H'H. 9368.		E, H'H. 9369.	
	Pit. %.	Ratio Core : Pit.	Pit. %.	Ratio Core : Pit.	Pit. %.	Ratio Core : Pit.
Carbon . . . .	0.060	1.33	0.051	3.31	0.047	1.96
Manganese . . . .	0.540	1.09	0.658	1.16	0.445	1.65
Phosphorus . . . .	0.048	1.91	0.082	2.51	0.046	2.71
Sulphur . . . .	0.026	2.27	0.032	2.88	0.035	3.69
Silicon . . . .	0.005	0.40	0.001	3.00	0.002	1.50
Nitrogen . . . .	0.016	...	0.017	1.18	0.015	1.07

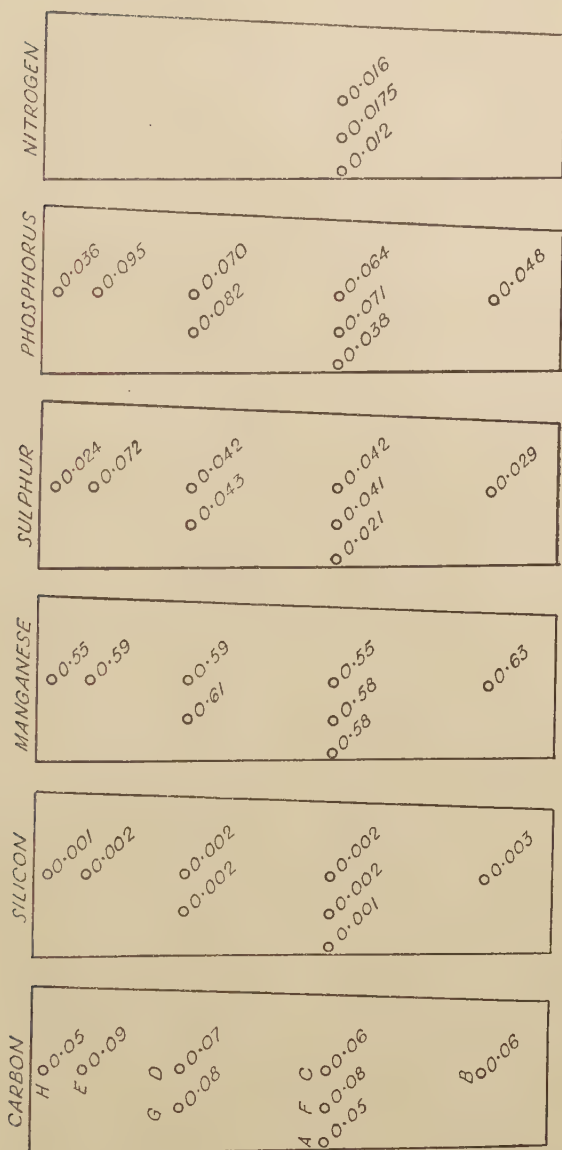


FIG. 4.—Ingots 64. Analytical Chart.





FIG. 5.—Ingot 9368 (Cast No. 4971). Analytical Chart.



FIG. 6.—Ingot 9369 (Cast No. 4943). Analytical Chart.

TABLE VI.—*Degree of Segregation at Middle of Ingots based on Analyses at Standard Positions.*

Positions : Ingot No. :	A : C, D.				A, G' : C, D.				A, G' : C, D.			
	64.				9368.				9369.			
Element.	Pit. %.	Ratio—			Pit. %.	Ratio—			Pit. %.	Ratio—		
		Rim : Pit.	Core : Pit.	Core : Rim.		Rim : Pit.	Core : Pit.	Core : Rim.		Rim : Pit.	Core : Pit.	Core : Rim.
Carbon .	0.060	0.83	1.08	1.30	0.051	0.84	1.80	2.16	0.047	0.66	1.22	1.85
Manganese .	0.540	1.07	1.05	0.98	0.658	0.99	1.03	1.01	0.445	0.98	0.96	0.98
Phosphorus .	0.048	0.79	1.40	1.76	0.082	0.76	1.29	1.71	0.046	0.83	1.28	1.55
Sulphur .	0.026	0.81	1.62	2.00	0.032	0.72	1.31	1.83	0.035	0.69	1.29	1.87
Silicon .	0.005	0.20	0.40	2.00	0.001	2.00	2.00	1.00	0.002	1.50	1.00	0.67
Nitrogen .	0.016	0.75	1.00	1.33	0.017	0.65	0.82	1.27	0.015	0.60	0.80	1.33

Considering first the carbon distribution, in ingot 64 there is some segregation of carbon towards the top, but, generally, the carbon distribution is fairly uniform, whilst in ingots 9368 and 9369 there is a considerable carbon segregation in the mid-portion of the ingot and even greater segregation towards the top.

The figures for manganese in all three ingots show very little segregation as compared with the pit analyses, with the exception of the top portions of ingots 9368 and 9369, although in the former case the average figure on which the ratio given in Table V. is calculated may be slightly misleading. There appears to be no direct relationship between these manganese figures and the sulphur present, and it is possible that the high manganese values at various points at the top of ingots 9368 and 9369 have their origin in coalesced oxides.

The degree of segregation of both phosphorus and sulphur in the middle portions of the ingot is lower in ingots 9368 and 9369 than it is in ingot 64, but in the top portion this relationship is reversed. The inference would appear to be that there has been greater movement of these impurities during the solidification process in 9368 and 9369 than in 64.

One other interesting point is shown by the analyses at the modified standard positions. In ingot 9368 there is a well-defined build-up of segregate at the junction of the rim and core, but this is not nearly so marked in ingot 9369 (compare analyses at positions *G* and *F* with *D* and *C*). This observation is confirmed in the detailed analyses of the section, discussed later.

One further general observation may be offered on the ratios shown in Tables V. and VI. It would appear that for a fairly wide range of rimming conditions the degree of separation of the segregating elements which may be expected is of the same order in all cases.

(4) *Detailed Analyses of Strips at the Middle of the Ingot Length.*

The method of examination employed for the analyses of these strips in ingot 64 was to cut a strip 2 in.  $\times$  1 in., the 1-in. face corresponding to the longitudinal section of the ingot. This bar was then milled for analysis, by  $\frac{1}{32}$ -in. steps, whilst the oxygen figures were obtained on approximately  $\frac{1}{2}$ -in. samples on the corresponding half of the ingot width.

In the case of ingots 9368 and 9369, the analyses and vacuum fusion determinations were made on two adjacent 1-in. bars from the same side of the ingot section, the general analyses again being done on  $\frac{1}{32}$ -in. samples and the oxygen on  $\frac{1}{2}$ -in. samples.

The analyses of the various cuts for ingot 64 are given in Table II. (pp. 18-19) of the Seventh Report, whilst the oxygen figures are given in Table II. (p. 22) of the Ninth Report.<sup>1</sup> The analyses for ingots 9368 and 9369 are given in Tables VII. and VIII. of this paper, and the vacuum fusion determinations for the oxygen and nitrogen in Tables IX. and X. (The hydrogen, nickel and arsenic figures have been tabulated only for ingot 9368.)

The results are shown in graphical form for all three ingots in Fig. 7. For purposes of record, Vickers hardness numbers for ingots 9368 and 9369 are also shown in Fig. 7 (*see* p. 320 P).

The curves, except for oxygen and nitrogen, have been drawn from point to point and not as smooth curves. It is considered that this is justified, as the experimental analytical error is low and the minor peaks and hollows represent genuine secondary segregation.

The point of junction between rim and core is indicated for each ingot on Fig. 7. In the section from ingot 64 the junction is at 5.25 in. and the accompanying unsoundness runs into the core for about 0.5 in. In ingot 9368 the junction is at 4.3 in., and the unsound area extends for almost 1 in. into the core in this particular step. In ingot 9369 the junction is at 4.1 in., and the unsound zone is about 0.8 in. wide inwards from that point.

Considering the results, generally, it will be noted that the major breaks in all graphs, when they occur, coincide with the junction and its accompanying unsound areas.

The following summary covers the more important observations which can be made regarding the variation in the percentage of the different elements across the ingot face :

*Carbon.*

*Ingot 64.*—Slight but definite fall from outside towards the junction. Junction region with sharp rise to a peak above the average. Core fairly uniform and above the pit analysis.

<sup>1</sup> Seventh and Ninth Reports on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1937 and 1939, *Special Reports* Nos. 16 and 27.

TABLE VII.—*Analyses of Denain Basic Bessemer Steel Ingot No. 9368 from Surface to Centre at Middle of Ingot.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N. %.	Hardness V.P.N.
1	0.083	...	...	0.188	...	...	0.017	...
2	...	0.035	0.699	...	...	...	...	205
3	...	...	...	...	0.034	0.051	...	...
4	0.079	...	...	0.044	...	...	0.016	164
5	...	0.033	0.719	...	...	...	...	...
6	...	...	...	...	0.033	0.052	...	142
7	0.075	...	...	0.050	...	...	0.015	...
8	...	0.031	0.685	...	...	...	...	133
9	...	...	...	...	0.033	0.046	...	...
10	0.077	...	...	0.055	...	...	0.016	129
11	...	0.031	0.692	...	...	...	...	...
12	...	...	...	...	0.033	0.045	...	129
13	0.075	...	...	0.055	...	...	0.015	...
14	...	0.030	0.688	...	...	...	...	132
15	...	...	...	...	0.032	0.045	...	...
16	0.076	...	...	0.055	...	...	0.016	143
17	...	0.028	0.688	...	...	...	...	...
18	...	...	...	...	0.033	0.044	...	142
19	0.074	...	...	0.050	...	...	0.015	...
20	...	0.027	0.696	...	...	...	...	130
21	...	...	...	...	0.032	0.045	...	...
22	0.076	...	...	0.049	...	...	0.015	130
23	...	0.027	0.696	...	...	...	...	...
24	...	...	...	...	0.032	0.047	...	131
25	0.072	...	...	0.048	...	...	0.014	...
26	...	0.027	0.696	...	...	...	...	133
27	...	...	...	...	0.032	0.046	...	...
28	0.069	...	...	0.047	...	...	0.014	131
29	...	0.027	0.696	...	...	...	...	...
30	...	...	...	...	0.035	0.045	...	129
31	0.071	...	...	0.049	...	...	0.015	...
32	...	0.027	0.696	...	...	...	...	...
33	...	...	...	...	0.035	0.047	...	129
34	0.064	...	...	0.052	...	...	0.015	...
35	...	0.027	0.681	...	...	...	...	124
36	...	...	...	...	0.038	0.047	...	...
37	0.065	...	...	0.047	...	...	0.015	133
38	...	0.027	0.696	...	...	...	...	...
39	...	...	...	...	0.041	0.046	...	132
40	0.067	...	...	0.047	...	...	0.015	...
41	...	0.027	0.696	...	...	...	...	125
42	...	...	...	...	0.038	0.045	...	...
43	0.067	...	...	0.049	...	...	0.015	128
44	...	0.027	0.696	...	...	...	...	...
45	...	...	...	...	0.041	0.045	...	126
46	0.063	...	...	0.050	...	...	0.015	...
47	...	0.028	0.703	...	...	...	...	124
48	...	...	...	...	0.043	0.042	...	...
49	0.066	...	...	0.057	...	...	0.015	124
50	...	0.027	0.703	...	...	...	...	...
51	...	...	...	...	0.040	0.041	...	122
52	0.067	...	...	0.059	...	...	0.015	...



TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>2</sub> . %.	Hardness V.P.N.
53	...	0.026	0.703	...	...	...	...	123
54	...	...	...	...	0.041	0.042	...	...
55	0.066	...	...	0.050	...	...	0.015	124
56	...	0.025	0.688	...	...	...	...	...
57	...	...	...	...	0.041	0.041	...	123
58	0.063	...	...	0.050	...	...	0.015	...
59	...	0.024	0.681	...	...	...	...	126
60	...	...	...	...	0.042	0.041	...	...
61	0.067	...	...	0.052	...	...	0.013	121
62	...	0.024	0.696	...	...	...	...	...
63	...	...	...	...	0.038	0.041	...	120
64	0.064	...	...	0.052	...	...	0.015	...
65	...	0.026	0.688	...	...	...	...	...
66	...	...	...	...	0.039	0.042	...	118
67	0.068	...	...	0.056	...	...	0.014	...
68	...	0.024	0.683	...	...	...	...	123
69	...	...	...	...	0.040	0.041	...	...
70	0.066	...	...	0.059	...	...	0.015	123
71	...	0.026	0.683	...	...	...	...	...
72	...	...	...	...	0.040	0.040	...	127
73	0.066	...	...	0.056	...	...	0.015	...
74	...	0.024	0.688	...	...	...	...	131
75	...	...	...	...	0.042	0.046	...	...
76	0.063	...	...	0.057	...	...	0.015	132
77	...	0.024	0.688	...	...	...	...	...
78	...	...	...	...	0.044	0.047	...	123
79	0.066	...	...	0.056	...	...	0.013	...
80	...	0.024	0.688	...	...	...	...	132
81	...	...	...	...	0.041	0.047	...	...
82	0.064	...	...	0.057	...	...	0.014	123
83	...	0.023	0.664	...	...	...	...	...
84	...	...	...	...	0.038	0.042	...	123
85	0.064	...	...	0.059	...	...	0.015	...
86	...	0.023	0.664	...	...	...	...	123
87	...	...	...	...	0.039	0.042	...	...
88	0.065	...	...	0.061	...	...	0.014	122
89	...	0.023	0.664	...	...	...	...	...
90	...	...	...	...	0.037	0.042	...	123
91	0.064	...	...	0.058	...	...	0.013	...
92	...	0.025	0.657	...	...	...	...	...
93	...	...	...	...	0.039	0.043	...	118
94	0.064	...	...	0.057	...	...	0.013	...
95	...	0.023	0.657	...	...	...	...	124
96	...	...	...	...	0.037	0.042	...	...
97	0.064	...	...	0.057	...	...	0.014	122
98	...	0.024	0.659	...	...	...	...	...
99	...	...	...	...	0.040	0.043	...	...
100	0.065	...	...	0.058	...	...	0.014	119
101	...	0.024	0.651	...	...	...	...	...
102	...	...	...	...	0.042	0.041	...	121
103	0.062	...	...	0.064	...	...	0.014	...
104	...	0.023	0.644	...	...	...	...	118
105	...	...	...	...	0.039	0.042	...	...
106	0.064	...	...	0.052	...	...	0.015	114

TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>2</sub> . %.	Hardness V.P.N.
107	...	0.025	0.644	...	...	...	...	...
108	...	...	...	...	0.040	0.040	...	122
109	0.065	...	...	0.055	...	...	0.014	...
110	...	0.023	0.644	...	...	...	...	118
111	...	...	...	...	0.040	0.043	...	...
112	0.067	...	...	0.049	...	...	0.013	124
113	...	0.025	0.644	...	...	...	...	...
114	...	...	...	...	0.042	0.043	...	105
115	0.064	...	...	0.051	...	...	0.015	...
116	...	0.025	0.659	...	...	...	...	121
117	...	...	...	...	0.041	0.043	...	...
118	0.062	...	...	0.049	...	...	0.014	120
119	...	0.023	0.636	...	...	...	...	...
120	...	...	...	...	0.041	0.042	...	123
121	0.064	...	...	0.052	...	...	0.013	...
122	...	0.024	0.644	...	...	...	...	120
123	...	...	...	...	0.043	0.041	...	...
124	0.068	...	...	0.052	...	...	0.014	119
125	...	0.023	0.651	...	...	...	...	...
126	...	...	...	...	0.042	0.043	...	120
127	0.069	...	...	0.049	...	...	0.015	...
128	...	0.022	0.666	...	...	...	...	119
129	...	...	...	...	0.043	0.044	...	...
130	0.071	...	...	0.053	...	...	0.014	121
131	...	0.025	0.673	...	...	...	...	...
132	...	...	...	...	0.043	0.044	...	...
133	0.075	...	...	0.057	...	...	0.015	119
134	...	0.028	0.673	...	...	...	...	...
135	...	...	...	...	0.041	0.049	...	130
136	0.084	...	...	0.067	...	...	0.017	...
137	...	0.032	0.665	...	...	...	...	128
138	...	...	...	...	0.038	0.052	...	...
139	0.097	...	...	0.078	...	...	0.018	127
140	...	0.039	0.692	...	...	...	...	...
141	...	...	...	...	0.038	0.057	...	132
142	0.105	...	...	0.078	...	...	0.018	...
143	...	0.040	0.718	...	...	...	...	147
144	...	...	...	...	0.037	0.057	...	...
145	0.107	...	...	0.086	...	...	0.018	151
146	...	0.043	0.718	...	...	...	...	...
147	...	...	...	...	0.038	0.058	...	154
148	0.102	...	...	0.083	...	...	0.018	...
149	...	0.041	0.712	...	...	...	...	173
150	...	...	...	...	0.042	0.057	...	...
151	0.118	...	...	0.095	...	...	0.019	187
152	...	0.045	0.718	...	...	...	...	...
153	...	...	...	...	0.044	0.064	...	177
154	0.128	...	...	0.106	...	...	0.021	...
155	...	0.048	0.718	...	...	...	...	165
156	...	...	...	...	0.041	0.072	...	...
157	0.137	...	...	0.104	...	...	0.020	151
158	...	0.052	0.725	...	...	...	...	...
159	...	...	...	...	0.044	0.073	...	189
160	0.143	...	...	0.104	...	...	0.021	...

TABLE VII.—*Continued.*

No.	P. %	S. %	Mn. %	C. %	Ni. %	As. %	N <sub>2</sub> . %	Hardness V.P.N.
161	...	0.057	0.712	...	...	...	...	143
162	...	...	...	...	0.042	0.073	...	...
163	0.163	...	...	0.115	...	...	0.021	143
164	...	0.071	0.725	...	...	...	...	...
165	...	...	...	...	0.043	0.077	...	...
166	0.154	...	...	0.119	...	...	0.022	140
167	...	0.067	0.705	...	...	...	...	...
168	...	...	...	...	0.043	0.066	...	140
169	0.135	...	...	0.113	...	...	0.021	...
170	...	0.052	0.705	...	...	...	...	140
171	...	...	...	...	0.042	0.064	...	...
172	0.119	...	...	0.094	...	...	0.019	143
173	...	0.046	0.705	...	...	...	...	...
174	...	...	...	...	0.041	0.060	...	140
175	0.112	...	...	0.091	...	...	0.019	...
176	...	0.042	0.712	...	...	...	...	151
177	...	...	...	...	0.042	0.059	...	...
178	0.112	...	...	0.091	...	...	0.018	155
179	...	0.045	0.712	...	...	...	...	...
180	...	...	...	...	0.042	0.060	...	145
181	0.114	...	...	0.097	...	...	0.021	...
182	...	0.045	0.712	...	...	...	...	154
183	...	...	...	...	0.044	0.061	...	...
184	0.116	...	...	0.094	...	...	0.019	143
185	...	0.049	0.705	...	...	...	...	...
186	...	...	...	...	0.043	0.061	...	144
187	0.119	...	...	0.093	...	...	0.019	...
188	...	0.048	0.705	...	...	...	...	131
189	...	...	...	...	0.043	0.062	...	...
190	0.119	...	...	0.087	...	...	0.020	134
191	...	0.049	0.705	...	...	...	...	...
192	...	...	...	...	0.043	0.061	...	139
193	0.119	...	...	0.091	...	...	0.019	...
194	...	0.048	0.705	...	...	...	...	136
195	...	...	...	...	0.042	0.061	...	...
196	0.119	...	...	0.085	...	...	0.019	143
197	...	0.049	0.680	...	...	...	...	...
198	...	...	...	...	0.044	0.059	...	...
199	0.114	...	...	0.087	...	...	0.019	137
200	...	0.048	0.668	...	...	...	...	...
201	...	...	...	...	0.045	0.067	...	137
202	0.112	...	...	0.091	...	...	0.018	...
203	...	0.042	0.668	...	...	...	...	137
204	...	...	...	...	0.044	0.064	...	...
205	0.111	...	...	0.089	...	...	0.018	134
206	...	0.044	0.680	...	...	...	...	...
207	...	...	...	...	0.046	0.063	...	131
208	0.115	...	...	0.089	...	...	0.018	...
209	...	0.045	0.660	...	...	...	...	133
210	...	...	...	...	0.043	0.059	...	...
211	0.115	...	...	0.089	...	...	0.018	131
212	...	0.044	0.661	...	...	...	...	...
213	...	...	...	...	0.046	0.065	...	132
214	0.113	...	...	0.090	...	...	0.018	...

TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>2</sub> . %.	Hardness V.P.N.
215	...	0.042	0.668	...	...	...	...	143
216	...	...	...	...	0.043	0.069	...	...
217	0.108	...	...	0.083	...	...	0.018	140
218	...	0.045	0.668	...	...	...	...	...
219	...	...	...	...	0.042	0.062	...	136
220	0.110	...	...	0.085	...	...	0.018	...
221	...	0.043	0.668	...	...	...	...	131
222	...	...	...	...	0.044	0.061	...	...
223	0.108	...	...	0.086	...	...	0.018	133
224	...	0.046	0.674	...	...	...	...	...
225	...	...	...	...	0.041	0.062	...	134
226	0.106	...	...	0.089	...	...	0.018	...
227	...	0.047	0.660	...	...	...	...	140
228	...	...	...	...	0.040	0.058	...	...
229	0.109	...	...	0.075	...	...	0.016	133
230	...	0.043	0.680	...	...	...	...	...
231	...	...	...	...	0.043	0.056	...	...
232	0.109	...	...	0.079	...	...	0.017	141
233	...	0.045	0.680	...	...	...	...	...
234	...	...	...	...	0.040	0.055	...	137
235	0.110	...	...	0.082	...	...	0.017	...
236	...	0.047	0.680	...	...	...	...	140
237	...	...	...	...	0.042	0.059	...	...
238	0.110	...	...	0.080	...	...	0.018	138
239	...	0.047	0.680	...	...	...	...	...
240	...	...	...	...	0.042	0.053	...	131
241	0.110	...	...	0.080	...	...	0.018	...
242	...	0.046	0.680	...	...	...	...	133
243	...	...	...	...	0.041	0.055	...	...
244	0.110	...	...	0.076	...	...	0.017	132
245	...	0.046	0.671	...	...	...	...	...
246	...	...	...	...	0.041	0.055	...	133
247	0.112	...	...	0.085	...	...	0.017	...
248	...	0.046	0.671	...	...	...	...	131
249	...	...	...	...	0.041	0.055	...	...
250	0.111	...	...	0.080	...	...	0.018	134
251	...	0.047	0.684	...	...	...	...	...
252	...	...	...	...	0.041	0.059	...	136
253	0.111	...	...	0.081	...	...	0.018	...
254	...	0.047	0.684	...	...	...	...	131
255	...	...	...	...	0.042	0.055	...	...
256	0.114	...	...	0.078	...	...	0.018	131
257	...	0.048	0.697	...	...	...	...	...
258	...	...	...	...	0.042	0.059	...	127
259	0.114	...	...	0.071	...	...	0.018	...
260	...	0.049	0.697	...	...	...	...	139
261	...	...	...	...	0.043	0.059	...	...
262	0.113	...	...	0.077	...	...	0.018	131
263	...	0.049	0.684	...	...	...	...	...
264	...	...	...	...	0.044	0.060	...	...
265	0.115	...	...	0.094	...	...	0.017	134
266	...	0.049	0.697	...	...	...	...	...
267	...	...	...	...	0.043	0.058	...	133
268	0.116	...	...	0.081	...	...	0.018	...

TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>2</sub> . %.	Hardness V.P.N.
269	...	0.049	0.677	...	...	...	...	133
270	...	...	...	...	0.042	0.060	...	...
271	0.116	...	...	0.089	...	...	0.018	130
272	...	0.048	0.670	...	...	...	...	...
273	...	...	...	...	0.041	0.060	...	140
274	0.116	...	...	0.078	...	...	0.018	...
275	...	0.048	0.684	...	...	...	...	133
276	...	...	...	...	0.043	0.061	...	...
277	0.111	...	...	0.078	...	...	0.018	128
278	...	0.047	0.677	...	...	...	...	...
279	...	...	...	...	0.042	0.062	...	...
280	0.117	...	...	0.076	...	...	0.017	128
281	...	0.048	0.677	...	...	...	...	...
282	...	...	...	...	0.033	0.072	...	134
283	0.115	...	...	0.079	...	...	0.018	...
284	...	0.045	0.690	...	...	...	...	130
285	...	...	...	...	0.035	0.078	...	...
286	0.112	...	...	0.075	...	...	0.018	129
287	...	0.045	0.677	...	...	...	...	...
288	...	...	...	...	0.039	0.077	...	133
289	0.110	...	...	{ 0.090	...	...	0.019	...
290	...	0.046	0.677	{ 0.090	...	...	...	128
291	...	...	...	...	0.038	0.071	...	...
292	0.114	...	...	0.085	...	...	0.018	128
293	...	0.045	0.684	...	...	...	...	...
294	...	...	...	...	{ 0.029	0.071	...	130
295	0.116	...	...	0.076	...	...	0.018	...
296	...	0.047	0.690	...	...	...	...	135
297	...	...	...	...	{ 0.029	0.065	...	...
298	0.113	...	...	0.075	...	...	0.018	...
299	...	0.047	0.703	...	...	...	...	135
300	...	...	...	...	0.030	0.065	...	...
301	0.116	...	...	0.075	...	...	0.020	135
302	...	0.048	0.697	...	...	...	...	...
303	...	...	...	...	0.030	0.063	...	130
304	0.113	...	...	0.075	...	...	0.020	...
305	...	0.046	0.697	...	...	...	...	128
306	...	...	...	...	0.038	0.093	...	...
307	...	...	...	0.090	...	...	0.018	127
308	...	...	0.663	...	...	...	...	...
309	...	...	...	...	0.041	...	...	130
310	0.106	...	...	0.081	...	...	0.019	...
311	...	0.041	0.656	...	...	...	...	130
312	...	...	...	...	0.038	0.060	...	...
313	0.106	...	...	0.081	...	...	0.018	130
314	...	0.042	0.661	...	...	0.081	...	...
315	...	...	...	...	0.035	0.090	...	131
316	0.108	...	...	0.087	...	...	0.018	...
317	...	...	0.661	...	...	...	...	130
318	...	...	...	...	0.035	0.070	...	...
319	0.109	...	...	0.081	...	...	0.018	130



TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>2</sub> . %.	Hardness V.P.N.
320	...	0.043	0.650	...	...	...	...	...
321	...	...	...	...	0.040	...	...	132
322	0.107	...	...	0.080	...	...	0.019	...
323	...	0.043	0.650	...	...	...	...	128
324	...	...	...	...	0.042	0.071	...	...
325	0.114	...	...	0.082	...	...	0.019	126
326	...	0.046	0.681	...	...	...	...	...
327	...	...	...	...	0.044	0.075	...	125
328	0.116	...	...	0.080	...	...	0.018	...
329	...	0.050	0.675	...	...	...	...	125
330	...	...	...	...	0.038	0.070	...	...
331	0.114	...	...	0.087	...	...	0.018	...
332	...	0.048	0.687	...	...	...	...	124
333	...	...	...	...	0.043	0.070	...	...
334	0.109	...	...	0.090	...	...	0.018	125
335	...	0.047	0.702	...	...	...	...	...
336	...	...	...	...	0.045	0.066	...	124
337	0.109	...	...	0.075	...	...	0.018	...
338	...	0.047	0.681	...	...	...	...	128
339	...	...	...	...	0.041	0.065	...	...
340	0.108	...	...	0.085	...	...	0.017	127
341	...	0.045	0.687	...	...	...	...	...
342	...	...	...	...	0.048	0.067	...	125
343	0.107	...	...	0.071	...	...	0.017	...
344	...	0.042	0.681	...	...	...	...	127
345	...	...	...	...	0.047	0.067	...	...
346	0.103	...	...	0.090	...	...	0.018	126
347	...	0.045	0.681	...	...	...	...	...
348	...	...	...	...	0.042	0.066	...	125
349	0.106	...	...	0.076	...	...	0.018	...
350	...	0.044	0.687	...	...	...	...	127
351	...	...	...	...	0.046	0.067	...	...
352	0.110	...	...	0.070	...	...	0.018	126
353	...	0.044	0.681	...	...	...	...	...
354	...	...	...	...	0.040	0.065	...	126
355	0.108	...	...	0.086	...	...	0.018	...
356	...	0.043	0.681	...	...	...	...	126
357	...	...	...	...	0.047	0.066	...	...
358	0.109	...	...	0.072	...	...	0.018	124
359	...	0.045	0.694	...	...	...	...	...
360	...	...	...	...	0.040	0.066	...	126
361	0.106	...	...	0.075	...	...	0.017	...
362	...	0.045	0.694	...	...	...	...	125
363	...	...	...	...	0.047	0.067	...	...
364	0.108	...	...	0.080	...	...	0.017	...
365	...	0.040	0.675	...	...	...	...	126
366	...	...	...	...	0.040	0.063	...	...
367	0.105	...	...	0.071	...	...	0.018	127
368	...	0.045	0.675	...	...	...	...	...
369	...	...	...	...	0.043	0.065	...	128
370	0.109	...	...	0.083	...	...	0.018	...
371	...	0.044	0.688	...	...	...	...	126
372	...	...	...	...	0.048	0.062	...	...
373	0.105	...	...	0.080	...	...	0.019	128

TABLE VII.—*Continued.*

No.	P. %.	S. %.	Mn. %.	C. %.	Ni. %.	As. %.	N <sub>a</sub> . %.	Hardness V.P.N.
374	...	0.046	0.688	...	...	...	...	...
375	...	...	...	...	0.046	0.061	...	127
376	0.106	...	...	0.083	...	...	0.018	...
377	...	0.045	0.675	...	...	...	...	129
378	...	...	...	...	0.046	0.061	...	...
379	0.106	...	...	0.078	...	...	0.018	130
380	...	0.044	0.688	...	...	...	...	...
381	...	...	...	...	0.045	0.061	...	129
382	0.108	...	...	0.077	...	...	0.019	...
383	...	0.044	0.694	...	...	...	...	127
384	...	...	...	...	0.046	0.061	...	...
385	0.111	...	...	0.080	...	...	0.019	130
386	...	0.042	0.688	...	...	...	...	...
387	...	...	...	...	0.043	0.062	...	128
388	0.104	...	...	0.083	...	...	0.019	...
389	...	0.044	0.688	...	...	...	...	128
390	...	...	...	...	0.041	0.062	...	...
391	0.109	...	...	0.077	...	...	0.018	129
392	...	0.043	0.694	...	...	...	...	...
393	...	...	...	...	0.046	0.065	...	130
394	0.107	...	...	0.074	...	...	0.019	...
395	...	0.045	0.707	...	...	...	...	128
396	...	...	...	...	0.046	0.064	...	...
397	0.109	...	...	0.094	...	...	0.018	...
398	...	0.044	0.694	...	...	...	...	...

*Ingot 9368.*—Abnormally high outside sample (probably due to carburisation by mould wash), and thereafter reasonably uniform until peak at junction. Core uniform above pit analysis figure.

*Ingot 9369.*—Slight fall in first inch. Tendency to rise towards junction. Only one peak sample at junction, after which core is uniform at about the same level as last inch before junction, the figure being just below pit analysis.

#### *Manganese.*

*Ingot 64.*—Slight fall towards middle of rim, followed by a gentle rise to junction, and uniform thereafter through core.

*Ingot 9368.*—A steady fall through rim, to a rise at junction; thereafter the core is somewhat irregular, but, in general, lower than the junction percentage.

*Ingot 9369.*—Gradual fall through rim. Very slight increase at junction followed by uniform manganese, except for one abnormal peak through core.

#### *Sulphur.*

*Ingot 64.*—Steady fall throughout rim with sharp rise at junction, followed by a gradual fall broken by one peak through core.

TABLE VIII.—*Analyses of Denain Basic Bessemer Steel Ingot No. 9369 from Surface to Centre at Middle of Ingot.*

No.	Weight. G.	P. %.	S. %.	Mn. %.	C. %.
1	3.98	...	...	0.448	0.041
2	7.15	0.053	0.036	...	...
6	8.00	...	...	0.464	0.046
7	6.2	0.048	0.034	...	...
11	6.98	...	...	0.458	0.044
12	7.17	0.046	0.033	...	...
16	7.57	...	...	0.462	0.043
17	6.75	0.043	0.033	...	...
21	7.89	...	...	0.465	0.043
22	7.86	0.040	0.029	...	...
26	7.10	...	...	0.455	0.033
27	7.91	0.038	0.028	...	...
31	7.96	...	...	0.451	0.033
32	6.95	0.038	0.027	...	...
36	7.79	...	...	0.451	0.036
37	7.65	0.038	0.027	...	...
41	7.55	...	...	0.445	0.033
42	7.93	0.036	0.026	...	...
46	6.12	...	...	0.442	0.035
47	7.84	0.037	0.025	...	...
51	7.60	...	...	0.439	0.031
52	7.54	0.035	0.025	...	...
56	7.12	...	...	0.435	0.032
57	7.68	0.033	0.025	...	...
61	7.54	...	...	0.429	0.034
62	6.17	0.033	0.025	...	...
66	7.52	...	...	0.433	0.032
67	7.41	0.033	0.023	...	...
71	8.17	...	...	0.420	0.033
72	7.61	0.034	0.024	...	...
76	7.44	...	...	0.417	0.039
77	7.22	0.034	0.023	...	...
81	6.96	...	...	0.417	0.038
82	7.62	0.034	0.024	...	...
86	7.01	...	...	0.414	0.030
87	7.08	0.035	0.023	...	...
91	7.44	...	...	0.407	...
92	7.60	0.035	0.025	...	...
96	8.19	...	...	0.407	0.033
97	7.96	0.036	0.025	...	...
101	6.94	...	...	0.406	0.034
102	6.80	0.036	0.026	...	...
106	7.02	...	...	0.406	0.030
107	6.79	0.038	0.024	...	...
111	7.95	...	...	0.406	0.029
112	7.87	0.036	0.026	...	...
116	6.86	...	...	0.406	0.029
117	5.92	0.038	0.030	...	...
121	6.76	...	...	0.397	0.032
122	4.96	0.038	0.033	...	...
126	7.96	...	...	0.406	0.045
127	7.48	0.049	{ 0.034 0.034	...	...

TABLE VIII.—*Continued.*

No.	Weight. G.	P. %.	S. %.	Mn. %.	C. %.
131	6.28	...	...	0.413	0.041
132	6.79	0.053	0.039	...	...
136	6.63	...	...	0.413	0.044
137	7.10	0.064	0.051	...	...
141	7.05	...	...	0.413	0.043
142	7.15	0.063	0.053	...	...
146	7.09	...	...	0.425	0.050
147	7.14	0.064	0.054	...	...
151	6.99	...	...	0.425	0.048
152	6.23	0.067	0.061	...	...
156	6.43	...	...	0.413	0.073
157	7.02	0.064	0.060	...	...
161	6.64	...	...	0.407	0.047
162	6.00	0.062	0.055	...	...
166	6.80	...	...	0.425	0.046
167	7.19	0.063	0.057	...	...
171	6.99	...	...	0.416	0.047
172	6.61	0.063	0.055	...	...
176	7.93	...	...	0.424 *	0.049
177	6.79	0.062	0.058	...	...
181	3.82	...	...	0.432	0.045
182	4.73	0.062	0.058	...	...
186	6.36	...	...	0.425	0.043
187	7.77	0.063	0.054	...	...
191	5.60	...	...	0.425	0.041
192	8.15	0.066	0.056	...	...
196	6.97	...	...	0.410	0.044
197	9.29	0.063	0.053	...	...
201	7.46	...	...	0.410 *	{ 0.055
202	6.35	0.062	0.055	...	{ 0.054
206	6.90	...	...	0.420	{ 0.050
207	6.29	0.063	0.055	...	{ 0.048
211	6.80	...	...	0.407	...
212	7.26	0.060	0.053	...	0.046
216	7.77	...	...	0.419 *	...
217	7.34	0.060	0.053	...	0.047
221	8.29	...	...	0.413	...
222	7.80	0.057	0.052	...	0.046
226	7.40	...	...	0.429	...
227	7.19	0.060	0.051	...	0.043
231	6.28	...	...	0.429 *	...
232	7.50	0.059	0.051	...	0.045
236	7.72	...	...	0.413	...
237	7.88	0.059	0.052	...	0.045
241	7.34	...	...	0.417 *	...
242	7.13	0.061	0.050	...	0.048
246	7.46	...	...	0.636 *	...
247	7.58	0.057	0.048	...	0.042
251	7.61	...	...	0.417	...
252	7.81	0.056	0.050	...	0.040
256	7.22	...	...	0.413	...
257	6.78	0.056	0.051	...	0.046
				...	...

\* Determinations in duplicate.

TABLE VIII.—*Continued.*

No.	Weight. G.	P. %.	S. %.	Mn. %.	C. %.
261	6.52	...	...	0.419	{ 0.046 0.042
262	6.74	0.056	0.050	...	...
266	7.25	...	...	0.417	0.045
267	7.06	0.056	0.048	...	...
271	7.21	...	...	0.410	0.040
272	7.01	0.055	0.049	...	...
276	7.64	...	...	0.413	0.043
277	6.93	0.055	0.050	...	...
281	6.94	...	...	0.413	0.041
282	7.19	0.054	0.050	...	...
286	6.73	...	...	0.410 *	0.050
287	6.89	0.056	0.052	...	...
291	7.83	...	...	0.419	0.045
292	7.92	0.058	0.051	...	...
296	7.64	...	...	0.410	0.043
297	7.71	0.059	0.058	...	...
301	6.94	...	...	0.413	0.047
302	6.68	0.058	0.072	...	...
306	7.12	...	...	0.431 *	0.046
307	7.42	0.059	0.060	...	...
311	7.44	...	...	0.406	0.041
312	7.37	0.058	0.058	...	...
316	6.73	...	...	0.413	0.040
317	7.0	0.057	0.056	...	...
321	7.57	...	...	0.419	0.043
322	5.90	0.057	0.058	...	...
326	7.69	...	...	0.413	0.046
327	7.50	0.058	0.052	...	...
331	7.57	...	...	0.413	0.040
332	9.25	0.058	0.050	...	...
336	5.50	...	...	0.419	0.040
337	6.63	0.058	0.051	...	...
341	6.80	...	...	0.406	0.041
342	6.86	0.055	0.044	...	...
346	6.34	...	...	0.452 *	0.042
347	7.26	0.056	0.047	...	...
351	6.14	...	...	0.406	0.039
352	7.41	0.056	0.048	...	...
356	7.53	...	...	0.419	0.042
357	7.03	0.054	0.047	...	...
361	7.58	...	...	0.413	0.043
362	7.77	0.056	0.048	...	...
366	7.08	...	...	0.400	0.050
367	6.93	0.055	0.047	...	...
371	7.32	...	...	0.413	0.047
372	6.96	0.053	0.049	...	...
376	6.85	...	...	0.425	0.050
377	6.67	0.055	0.049	...	...
381	7.48	...	...	0.413	0.053
382	5.80	0.054	0.050	...	...

\* Determinations in duplicate.



TABLE IX.—*Vacuum Fusion Analyses of Samples taken across the Middle of Denain Ingot No. 9368.*

Samples taken every  $\frac{1}{2}$  in. from outside to centre of ingot section.  
 Samples Nos. 22, 23, 24 were spongy and contained rust.

Sample No.	Oxygen. %.	Nitrogen. %.	Hydrogen. Ml. per 100 g.
1 outside	0.035	0.016	0.85
2	0.032	0.014	...
3	0.034	0.013	2.70
4	0.032	0.012	1.70
5	0.024	0.010 <sub>4</sub>	...
6	0.021	0.010 <sub>5</sub>	1.60
7	0.013	0.010 <sub>8</sub>	3.05
8	0.010 <sub>3</sub>	0.013	1.15
9	0.013	0.016	0.50
10	0.016	0.020	0.75
11	0.012	0.018	1.30
12	0.012	0.019	1.40
13	0.012	0.019	1.90
14	0.012 <sub>5</sub>	0.017	1.90
15	0.012 <sub>5</sub>	0.017	2.25
16	0.012	0.018	0.90
17	0.012	0.018	0.50
18	0.011 <sub>5</sub>	0.017	1.75
19	0.013	0.016	1.05
20	0.014	0.017	2.00
21	0.018	0.017	3.35
22	0.029	0.018	5.30
23	0.062	0.019	15.10
24 centre	0.085	0.018	26.30

TABLE X.—*Total Oxygen and Nitrogen Contents of Samples taken across the Middle of Denain Ingot No. 9369.*

Samples taken every  $\frac{1}{2}$  in. from outside to centre of ingot section.

Sample No.	Oxygen. %.	Nitrogen. %.	Sample No.	Oxygen. %.	Nitrogen. %.
1 outside	0.043 <sub>5</sub>	0.013	14	0.042	0.014 <sub>5</sub>
2	0.043	0.011 <sub>5</sub>	15	0.042 <sub>5</sub>	0.014 <sub>5</sub>
3	0.040 <sub>5</sub>	0.011	16	{ 0.042	0.015
4	0.038	0.010		{ 0.040	0.014
5	{ 0.038 <sub>5</sub>	...	17	0.042	0.014
	{ 0.037 <sub>5</sub>	0.009 <sub>5</sub>	18	0.042	0.014 <sub>5</sub>
6	0.037 <sub>5</sub>	0.009 <sub>5</sub>	19	0.041 <sub>5</sub>	0.014
7	0.034 <sub>5</sub>	0.009 <sub>5</sub>	20	0.041	0.014 <sub>5</sub>
8	0.032 <sub>5</sub>	0.010	21	{ 0.048 <sub>5</sub>	0.014 <sub>5</sub>
9	0.040 <sub>5</sub>	0.014		{ 0.040	0.014 <sub>5</sub>
10	0.043 <sub>5</sub>	0.015 <sub>5</sub>	22	{ 0.046	0.014
11	0.043	0.014 <sub>5</sub>		{ 0.047 <sub>5</sub>	0.014
12	0.044	0.015	23	0.042	0.014 <sub>5</sub>
13	{ 0.040 <sub>5</sub>	0.015 <sub>5</sub>	24 centre	0.038 <sub>5</sub>	0.013 <sub>5</sub>
	{ 0.046	0.015 <sub>5</sub>			

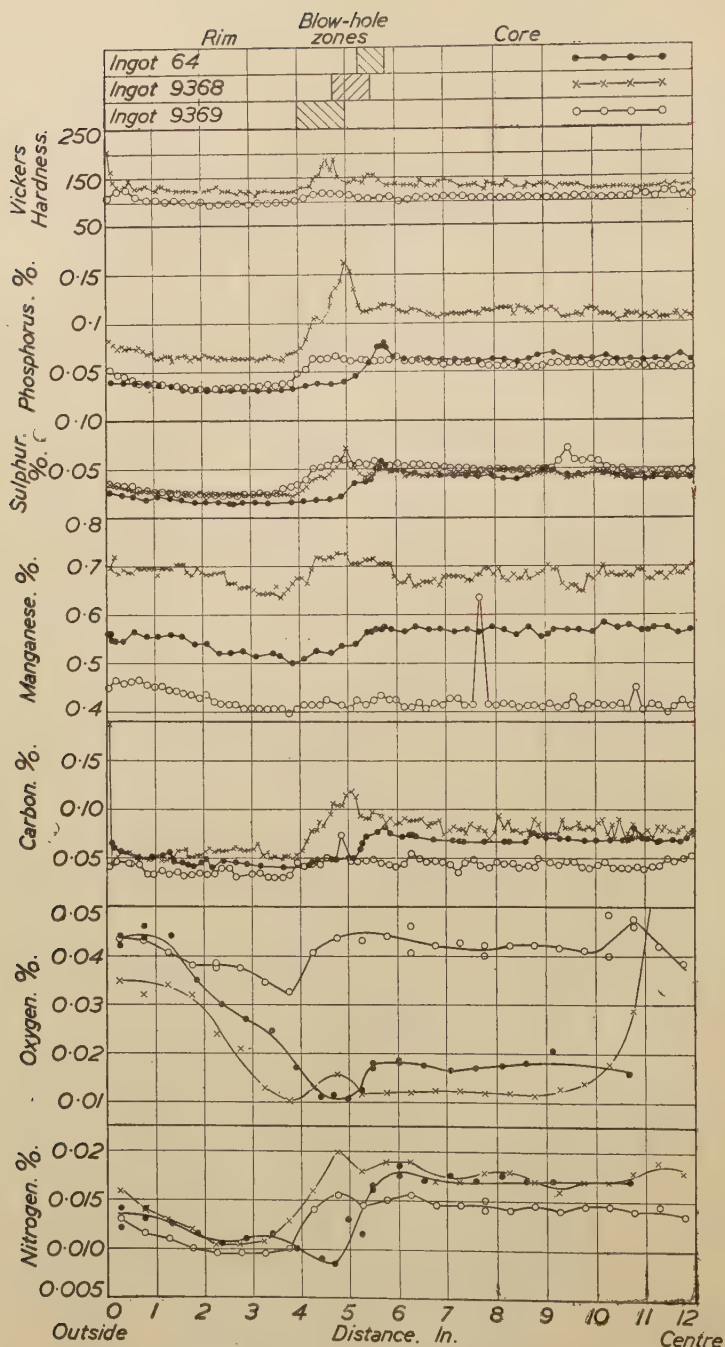


FIG. 7.—Analyses of Strips from Ingots 64, 9368 and 9369.

*Ingot 9368.*—Gentle fall through rim, followed by sharp rise at junction and by reasonably uniform core below junction peak.

*Ingot 9369.*—Slight fall in first inch. Uniform through remainder of rim with a rise at junction and a continuation on junction level through core with one peak at position similar to that mentioned for ingot 64.

### *Phosphorus.*

*Ingot 64.*—Gradual fall through rim with a rise to a peak at junction, continuing, with the exception of one peak, at an average below junction peak.

*Ingot 9368.*—Slight fall in first inch of rim. Uniform thereafter until rise at junction. Fall from junction peak and uniform thereafter.

*Ingot 9369.*—Fall in first inch of rim. Uniform to junction, where it rises and continues without any junction peak. Uniform with, if anything, a slight fall towards the centre.

### *Oxygen.*

*Ingot 64.*—Decreases progressively in the rim; rises slightly at the junction and continues at a much lower value than in the rim.

*Ingot 9368.*—Similar to ingot 64, except that, having risen to a peak at the junction, it falls again to a low level and continues uniform, probably rising slightly towards the centre.

*Ingot 9369.*—Falls throughout the rim, but not so sharply as in ingot 64 and ingot 9368. It rises at the junction and continues at a higher level than the rim average (at approximately the same figure as the first inch from the outside) and finally, unlike ingots 64 and 9368, appears to fall again towards the centre.

### *Nitrogen.*

*Ingot 64.*—Falls throughout the rim, rises sharply at the junction and continues uniform at a level above the rim average.

*Ingot 9368.*—Falls gently through the rim, rises at the junction and continues fairly uniform at an average above the rim figure.

*Ingot 9369.*—Similar to ingot 9368, but there is not the same pronounced difference between the rim average and core.

All three ingots have this in common: There is a gradual diminution in the percentage of carbon, manganese, sulphur and phosphorus as one traverses the rim from the outside surface towards the junction zone. There is also in each ingot a discontinuity in the percentage of these elements at the junction zone, but, whereas in the case of ingots 64 and 9368 there is a sharp rise in the percentage of the various elements at the junction, which is not maintained at its peak throughout the core, in the case of

ingot 9369 the moderate rise which occurs represents a figure only slightly higher than the average percentage in the core itself. This suggests that, because of relative freedom from blow-holes in the junction zone or for some other reason, there has been no excessive build-up of impurity where the rim ceased to form. This result, which is confirmed so far as the absence of undue segregation at the junction is concerned by the analyses of the standard positions mentioned in the previous section, may be taken as one of the suggestive differences between 9369 and the other two ingots.

Turning now from the general form of the graphs to the actual figures which they represent, it is instructive to compare those for carbon, manganese, sulphur, phosphorus and nitrogen. Taking the pit analysis figure in each case as a datum line, it will be found that, in all cases, the phosphorus and sulphur of the rim, except perhaps on the extreme outside, are always lower than the pit figures, whilst the figures in the core are all higher than the pit figures, as is to be expected.

The graphs portraying composition in the first inch of rim suggest that, in the case of ingot 9369, more material of average (*i.e.*, pit) analysis was frozen in the extreme outside, presumably by chilling action, than in the other two cases.

The manganese graphs of the three ingots show some interesting differences. In ingot 64 and ingot 9369 the figures for the first 2 in. of the rim are above the pit figure, whilst in 9368, for the same relative position, the average is, if anything, below it. In ingot 64 the manganese continues below the pit figure in the rim but rises above it in the core, whilst in ingot 9369, with the exception of two points, the manganese is consistently below the pit figure, both in the remainder of the rim and throughout the core. The manganese figures for 9368 are extremely irregular. A small portion of the rim near the junction is below the pit figure and the remainder, although the figures vary considerably from point to point, is, in general, above it. The manganese results on ingot 9368 are surprisingly irregular when compared with those for the other two ingots. They reflect a general heterogeneity in the core which is greater than normal.

Carbon results on ingot 64 show a rim generally below the pit value with a core which, apart from the peak at the junction, is fairly regular but above it. In ingot 9368, leaving out the first sample, the rim figures coincide with the pit figures, but the core figures are above them. In ingot 9369 there is less carbon variation between rim and core than in the other two cases, and, in general, both parts of the ingot are below the pit figure, with the exception of one or two points. The rim, however, is again slightly lower than the core.

The oxygen curves are of very considerable interest, especially as far as the oxygen content is concerned. The first inch of the rim in ingots 64 and 9369 shows a similar oxygen content, whilst

9368 is considerably lower, but thereafter 64 follows in the general direction of 9368, whilst 9369, throughout the rim, decreases at a much slower rate. When the point of minimum oxygen content is reached, the 9369 figure is 0.032%, whilst those for 64 and 9368 are 0.01% and 0.011% respectively. In the core portion 9369 shows a uniformly high figure compared with the other two ingots, which continue, apart from slight variations, as already pointed out, on a low level. The average oxygen in the core portion, ignoring doubtful samples due to blow-holes, &c., for the three ingots is:

Ingot No.	64	9368	9369
Average oxygen	0.017%	0.013%	0.042%

The figures for nitrogen compared with the pit results show that the rim is, in all cases, below the pit figure and that the average for the core is, in general, equal to the pit figure.

### DISCUSSION OF RESULTS.

The data which have been assembled and made the subject of this comparative study could, no doubt, form the basis of an elaborate discussion on many of the various aspects—practical and theoretical—of the important subject of rimming steel. It is not the intention here, however, to do this in any detail, but only to discuss in broad general terms certain indications which are provided as to the factors that control the rimming process, and the light which is thrown on the mechanism of that process. It is justifiable on the evidence to regard ingot 9369 as a normal ingot and ingots 64 and 9368 as abnormal.

The works conditions prevailing during the blow from which ingot 64 was made were unusual. The converters were working only one shift of 8 hr. per day, and the conditions, generally, were such as to produce cold blowing. Further, bearing in mind these conditions and that the mixer metal contained only 0.34% of silicon and would almost certainly be cold, the actual blow itself was heavily scrapped before the converter was ever turned up for blowing. The time intervals during which the converter was not blowing after the metal had been run into the vessels make up an aggregate of unusually long duration. It can be taken as certain that this ingot is the product of a cold blow and that the factor of temperature bulked largely in the results obtained. This, of course, is confirmed by the observers' report that the ingots cast formed crusts of varying thickness on the surface as the metal rose in the moulds and that the particular ingots taken had to be specially treated by poking to keep the tops open. The casting temperature was given at 1480° C., which was the same as for ingot 9368 but some 40° below that for ingot 9369. The teeming time, although the same size of nozzle was used, was 25% greater than for the two blows from which the other ingots under consideration were made.

Ingots 9368 and 9369 were made from separate blows when



works conditions were more nearly normal. Actually, ingot 9369, correctly described by the observers as a perfect example of a rimming ingot, was obtained without any difficulty, but great difficulty was experienced in attempting to duplicate ingot 64. In the ultimate result, as can be seen by considering the data, ingot 9368 is, in some respects, intermediate between the perfect example (9369) and the very abnormal ingot 64, but it is not so clear that the abnormality of ingot 9368 is due to temperature causes. The casting temperature was certainly the same as for ingot 64, but it would seem that the deficient rimming properties are due, in part at least, to other causes. It is at this point that the significance of the oxygen results and the manganese content of the blown metal becomes apparent.

If one classifies roughly the mould action in the three cases, one has "no visible effervescence," "a small and sluggish initial effervescence" followed by rimming, and a "free effervescence" for ingots 64, 9368 and 9369, respectively. The finishing slags contained 11.7%, 4.1% and 7.29% of FeO and the pit manganese figures are 0.54%, 0.65% and 0.45%. It seems a fair inference that the absence of rimming action in ingot 64 was due to incorrect temperature, with the oxygen available immobilised by manganese. In ingot 9368, there was probably a deficiency of oxygen, and what there was became ineffective through the presence of excess manganese. In ingot 9369 the temperature, manganese content and oxygen percentage were all favourable.

It might be remarked, in passing, that to secure satisfactory rimming, it would not appear to be necessary to have excessive oxygen present. This is borne out by practical experience of the basic Bessemer process generally.

It will be seen from this survey that the metallurgical conditions necessary for vigorous mould effervescence are clearly indicated in the three cases under review, although actual practical limits cannot be definitely defined on such limited data. The conditions, as just noted, are correct temperature, low manganese and correct oxygen.

We may now proceed to consider what happens in the moulds during solidification, bearing in mind the metallurgical factors produced by the actual works practice, *i.e.*, the actual mechanics of the rimming process.

The comparative freedom from blow-holes in ingot 64 has already been commented upon. This seems almost certainly due to the fact that there was a deficiency of gas to form them, at least in the early stages of the freezing process. It seems likely that this particular ingot owes its relatively thick rim and top crust, which, in this case, may be regarded as part of the rim proper, to low temperature. The action by which the rim is formed would, therefore, be in the nature of selective freezing rather than the combined action of falling temperature and mechanical movement arising from effervescence. It is possible that there may have

been, at a late stage in the freezing, some evolution of gas, resulting in a mild effervescence, which would, however, be more or less suppressed by the top crust, but not before the mechanism of the operation has resulted in a structure similar to that of more normally rimmed material. A contributory factor in this process may have been the turbulence effected by the metal stream from the ladle.

Ingot 9368 appears to have been a case of delayed effervescence, due, as already suggested, to a deficiency of oxygen to produce the necessary action. The comparatively sluggish metal, due to the low temperature, led to the imprisonment of abnormally large quantities of gas in the rim and at the rim-core junction, and this explains the rising of the metal in the mould during the later stages of freezing and the arched top already noted. It also explains the relatively high degree of heterogeneity shown by the curves of core composition—particularly with regard to manganese.

The free action in ingot 9369 resulted in an ingot of very uniform texture in the core part, especially in the lower portions of the ingot. The excess gas was swept out, particularly at the junction of the rim and core. As already noted, the core appears to have settled down inside the rim after it was formed, which may be taken as evidence of an effervescing action continuing practically until the core solidified.

The V-shaped segregate at the very top of this core may possibly indicate a short period of quiescence during which the impurities segregated in the same manner as the primary segregate of a fully killed ingot. This implies that in the final stages of solidification the core did not freeze simultaneously as a whole. The collection of segregate in the core in this particular form is, however, abnormal, and its occurrence in this case may have been purely fortuitous. As a general rule, as is the case in ingot 9368, areas of extremely high concentrations of impurity in the core are found at the top of the core in a saucer-shaped form in the relatively unsound part immediately below the crust.

The effect of these various degrees of vigour in the rimming action certainly produced one important difference: The peaks in the composition shown at the junction of the rim and core are only evident in the two ingots in which rimming was deficient. Obviously, in the ingot in which rimming was sufficiently active, a greater degree of homogeneity was obtained throughout the core section.

A further consideration, arising from the evidence, justifies comment. The observers remarked on the considerable quantity of slag on the top of ingot 9369. It is clear that vigorous effervescence not only removes excessive gas and local concentrations of impurity, but it also assists in eliminating non-metallic products which would otherwise be entrained in the body of the ingot. Clean steel, therefore, so far as the term may be applied to rimmed steels, demands vigorous effervescence and adequate temperatures.

## CONCLUSIONS.

It is considered that this work has shown that :

(1) The temperature, state of oxidation and manganese content are the controlling factors in the rimming action.

(2) Vigorous effervescence reduces the tendency to excessive local segregation and assists in producing uniformity, as regards both composition and freedom from non-metallic impurity.

(3) Ingot structures may be obtained in unkilld steel which simulate in a remarkable degree the final structure of a properly rimmed ingot, even when the conditions are not favourable to correct rimming action.

## ACKNOWLEDGMENTS.

In addition to the thanks which are due to Monsieur Clerf for his assistance in procuring the ingots, the Ingot Committee and the author wish to express their indebtedness to Mr. A. G. Hock and Mr. R. H. Myers, who acted as observers at Denain when the ingots were made, and prepared full reports on the works practice employed; to Dr. W. H. Hatfield, F.R.S., and his staff, Brown-Firth Research Laboratories, for preparing macro-etchings and sulphur prints; to Dr. Swinden and his staff, Central Research Department, The United Steel Companies, Ltd., for vacuum fusion determinations and supervising the preparation of samples; and to Dr. H. A. Dickie and his staff, Department of Research and Technical Development, Messrs. Stewarts and Lloyds, Ltd., for analyses and help in numerous other ways.

[This paper was discussed jointly with the preceding one by D. Binnie on "An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process," and the three following by J. Mitchell on "Rimming Steel," by T. Swinden on "Rimming Steel," and by T. Swinden and W. W. Stevenson on "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C."]

## RIMMING STEEL.<sup>1</sup>

### REPORT ON FOUR INGOTS OF BASIC BESSEMER STEEL.

BY J. MITCHELL (MESSRS. STEWARTS AND LLOYDS, LTD.).

(Figs. 2 to 10 = Plates XXVIII. and XXIX.)

*Paper No. 14/1942 of the Committee on the Heterogeneity of Steel  
Ingots.*

#### SUMMARY.

A study has been made of four low-carbon basic Bessemer steel ingots of British manufacture—all cast from the same blow. As far as possible, the conditions of manufacture and examination were kept constant, in order that the effect of mould size might be studied. The data given include steelmaking practice, sulphur- and macro-prints of ingot sections and analyses of these sections at selected positions. These are reviewed in their relation to rimming-steel practice and theory.

#### *Introductory.*

AN exhaustive examination having been made of basic Bessemer steel ingots of Continental manufacture,<sup>2</sup> it was considered that a similar examination of British basic Bessemer steel ingots would be of interest. Through the courtesy of Messrs. Stewarts and Lloyds, Ltd., who provided them, the Committee on the Heterogeneity of Steel Ingots have had an opportunity of examining four ingots of different weights made at Corby from the same blow.

The record which follows may be regarded, therefore, as an extension, by the inclusion of the factor of ingot size, of the work which has already been done on low-carbon rimming steel ingots of basic Bessemer origin.

#### *Steelmaking Data.*

Particulars of the blow from which the ingots were made are given in Table I. It was considered to be representative of the practice normally employed at Corby in making low-carbon tube steel.

<sup>1</sup> Received October 27, 1942. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed are the author's, and are not necessarily endorsed by the Committee as a body.

<sup>2</sup> J. Mitchell, *Journal of The Iron and Steel Institute*, 1942, No. II., p. 295 P (this volume).

TABLE I.—*Steelmaking Data. Blow No. 8896.*

<i>Converter Charge.</i>		<i>Converter Slag Analysis.</i>		<i>Time Chart.</i>			
Iron 23 tons 0 cwt.		SiO <sub>2</sub>	5.54%	Fore-blow	Min.	Sec.	
Scrap 2500 lb.		FeO	9.07%	After-blow	9	0	
Lime 6500 lb.		Fe <sub>2</sub> O <sub>3</sub>	4.80%	Pouring	3	10	
<i>Converter Addition.</i>		Al <sub>2</sub> O <sub>3</sub>	1.51%	Standing time	1	15	
Spiegel 100 lb.		MnO	0.29%	(end of pouring to start of teeming)			
<i>Ladle Addition.</i>		CaO	53.65%	Pouring temp.*	4	0	
Fe-Mn (80%)		MgO	1.25%	Teeming temp.*	1630° C.		
320 lb.		CaS	0.101%		1570° C.		
<i>Soda Addition.</i>		SO <sub>3</sub>	0.017%				
112 lb. (to transfer ladle)		P <sub>2</sub> O <sub>5</sub>	22.82%				
		Fe	10.42%				
		P	9.965%				
		S	0.052%				
<i>Analyses.</i>							
		C. %.	Mn. %.	Si. %.	S. %.	P. %.	N <sub>2</sub> . %.
Iron to converter :		3.08	0.533	0.446	0.035	1.96	...
Blown metal		0.014	0.111	...	0.032	0.034	0.013
Pit ingot	$\left\{ \begin{array}{l} B \\ D \end{array} \right.$	0.055	0.491	...	0.030	0.043	0.013
samples	$\left\{ \begin{array}{l} D \\ E \end{array} \right.$	0.053	0.491	...	0.031	0.046	0.013
	$\left\{ \begin{array}{l} E \end{array} \right.$	0.056	0.491	...	0.033	0.046	0.013

Ingot.	Weight.		Teeming Time.		Aluminium Added.	Time of Solidification of Top.		Stripping Time.	Remarks.
	Tons.	Cwt.	Min.	Sec.	Oz.	Min.	Sec.	Hr. Min.	
A	4	5	2	40	4 $\frac{1}{4}$	23	0	1 35	Estimated ingot weight. Stood vertically till cold.
B	4	7†	2	35	4 $\frac{1}{4}$	25	0	1 34	Stood vertically till cold.
C	2	7†	1	35	2 $\frac{1}{2}$	22	0	1 34	Stood vertically till cold.
D	1	6†	1	5	1 $\frac{1}{2}$	22	0	1 35	Toppled during stripping.
E	3	2†	2	0	3	26	0	1 36	Stood vertically till cold.
F	4	5	2	40	4 $\frac{1}{4}$	24	0	1 37	Estimated ingot weight. Stood vertically till cold.
...	1	15	...	...	...	...	...	...	Estimated ingot weight. Scrap ingot.

## REMARKS.

Nozzle size, 1 $\frac{1}{4}$  in.

\* Temperatures taken with Bi-optix optical pyrometer.

† These ingots were taken for the Heterogeneity Committee.

Ladle skull, nil.

All moulds preheated by teeming an earlier blow, which remained 1 $\frac{1}{2}$  hr. before stripping. The moulds were then allowed to cool for 4 hr. before use for the special blow. At the time of teeming all moulds were hot.

*Aluminium addition to moulds.*—One ounce of aluminium per estimated ton was used for each ingot. Half this aluminium was added when the moulds were three-quarters full, and half when the moulds were four-fifths full. An extra  $\frac{1}{4}$  oz. of aluminium was added to the top of each ingot after the mould was full.



The ingots taken for examination were the second, third, fourth and fifth ingots teemed, and Fig. 1 is a drawing of the moulds used.

A quantity of aluminium, estimated to amount to 1 oz. per ton of steel, was added to the mould in each case during teeming.

The ingots were allowed to stand sufficiently long before stripping to ensure that they were completely solid, and they were kept in a vertical position until cold.

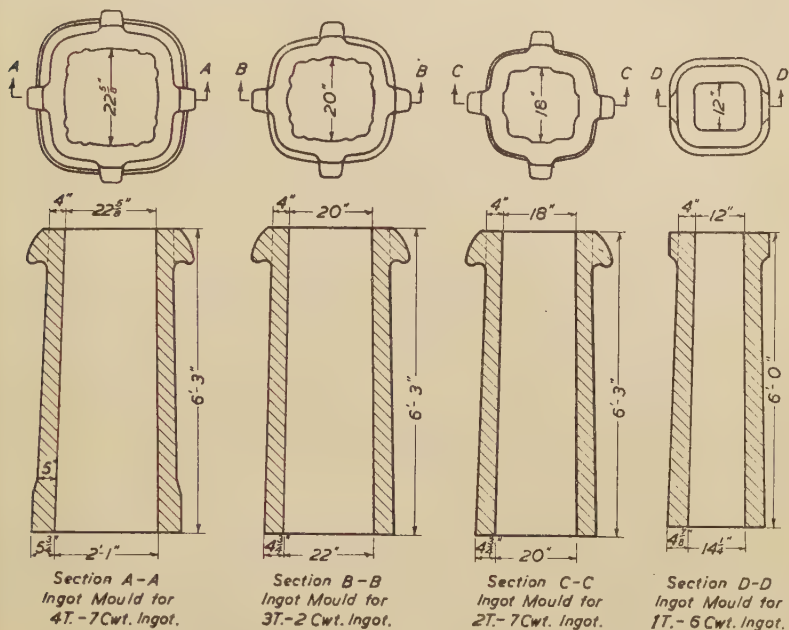


FIG. 1.—The Moulds in which the Four Ingots were Cast.

The weights shown in Table I. are actual weights, and for convenience the different ingots will be referred to throughout as 4-ton, 3-ton, 2-ton and 1-ton, respectively. The overall lengths were :

4-ton.	3-ton.	2-ton.	1-ton.
68 in.	70 in.	66 in.	73 in.

Fig. 2 is a photographic representation of the tops of the ingots.

### *Methods of Examination.*

The ingots were sectioned exactly on the central axis, and the results of a sulphur print and macro-etch for each ingot are shown in Figs. 3, 4, 5 and 6.

Bars 2 in.  $\times$  1 in. were then taken from the sectioned faces :

TABLE II.—*Analysis of Strips.**T, M, B* = top, middle and bottom of ingot, respectively.1 = outer edge of rim. 2 = inner edge of rim adjacent to junction zone.  
3 = inside core near core/rim junction. 4 = inside core at position midway between junction zone and centre of ingot.

No.	P. %.	S. %.	Mn. %.	C. %.	Cu. %.	Ni. %.	As. %.	O <sub>2</sub> . %.	N <sub>2</sub> . %.
<i>4.35-ton Ingot.</i>									
<i>T1</i>	0.035	0.022	0.491	0.066	0.006	0.035	0.034	0.042	0.009 <sub>5</sub>
<i>T2</i>	0.028	0.018	0.421	0.039	0.006	0.035	0.028	0.012 <sub>5</sub>	0.007
<i>T3</i>	0.066	0.050	0.494	0.086	0.007	0.036	0.051	0.026	0.015
<i>T4</i>	0.062	0.045	0.491	0.078	0.007	0.038	0.047	0.027	0.013 <sub>5</sub>
<i>M1</i>	0.032	0.025	0.494	0.052	0.006	0.035	0.029	0.043 <sub>5</sub>	0.009
<i>M2</i>	0.029	0.020	0.459	0.041	0.005	0.034	0.028	0.016	0.008
<i>M3</i>	0.069	0.055	0.484	0.083	0.008	0.039	0.051	0.025	0.014
<i>M4</i>	0.058	0.045	0.477	0.071	0.007	0.038	0.046	0.022	0.013 <sub>5</sub>
<i>B1</i>	0.037	0.026	0.506	0.059	0.006	0.033	0.034	0.045 <sub>5</sub>	0.010
<i>B2</i>	0.028	0.020	0.449	0.043	0.008	0.030	0.032	0.025	0.008
<i>B3</i>	0.052	0.036	0.456	0.059	0.008	0.036	0.041	0.025 <sub>5</sub>	0.013 <sub>5</sub>
<i>B4</i>	0.048	0.036	0.470	0.062	0.006	0.032	0.041	0.022 <sub>5</sub>	0.011
<i>3.1-ton Ingot.</i>									
<i>T1</i>	0.036	0.025	0.493	0.056	0.012	0.037	0.033	0.041	0.009
<i>T2</i>	0.032	0.020	0.431	0.036	0.007	0.038	0.032	0.011	0.007
<i>T3</i>	0.078	0.053	0.507	0.087	0.008	0.041	0.057	0.027	0.015 <sub>5</sub>
<i>T4</i>	0.084	0.067	0.500	0.098	0.008	0.043	0.053	0.023 <sub>5</sub>	0.013 <sub>5</sub>
<i>M1</i>	0.037	0.025	0.493	0.058	0.006	0.035	0.032	0.041	0.010 <sub>5</sub>
<i>M2</i>	0.035	0.022	0.445	0.042	0.007	0.036	0.033	0.016	0.008 <sub>5</sub>
<i>M3</i>	0.075	0.060	0.500	0.080	0.007	0.041	0.055	0.021	0.015
<i>M4</i>	0.065	0.052	0.480	0.067	0.008	0.040	0.051	0.020 <sub>5</sub>	0.013 <sub>5</sub>
<i>B1</i>	0.041	0.029	0.507	0.061	0.006	0.038	0.033	0.040 <sub>5</sub>	0.010 <sub>5</sub>
<i>B2</i>	0.037	0.024	0.452	0.051	0.007	0.038	0.031	0.026	0.008 <sub>5</sub>
<i>B3</i>	0.052	0.038	0.452	0.064	0.007	0.038	0.039	0.021 <sub>5</sub>	0.010 <sub>5</sub>
<i>B4</i>	0.050	0.038	0.438	0.061	0.007	0.039	0.039	0.021 <sub>5</sub>	0.011 <sub>5</sub>
<i>2.35-ton Ingot.</i>									
<i>T1</i>	0.036	0.024	0.506	0.058	0.007	0.030	0.032	0.044 <sub>5</sub>	0.009 <sub>5</sub>
<i>T2</i>	0.032	0.019	0.442	0.041	0.007	0.032	0.031	0.010	0.008
<i>T3</i>	0.072	0.055	0.509	0.089	0.009	0.032	0.054	0.020 <sub>5</sub>	0.014
<i>T4</i>	0.069	0.052	0.506	0.085	0.008	0.030	0.051	0.020 <sub>5</sub>	0.014
<i>M1</i>	0.038	0.028	0.548	0.060	0.007	0.026	0.030	0.043 <sub>5</sub>	0.010 <sub>5</sub>
<i>M2</i>	0.033	0.022	0.456	0.046	0.007	0.025	0.033	0.017	0.008
<i>M3</i>	0.072	0.056	0.506	0.082	0.010	0.034	0.055	0.022	0.014 <sub>5</sub>
<i>M4</i>	0.062	0.046	0.491	0.074	0.008	0.032	0.050	0.021 <sub>5</sub>	0.013 <sub>5</sub>
<i>B1</i>	0.036	0.027	0.497	0.064	0.006	0.034	0.032	0.043	0.010
<i>B2</i>	0.034	0.022	0.456	0.047	0.006	0.034	0.031	0.023 <sub>5</sub>	0.008
<i>B3</i>	0.047	0.035	0.463	0.059	0.006	0.034	0.041	0.023 <sub>5</sub>	0.011
<i>B4</i>	0.049	0.036	0.463	0.060	0.006	0.032	0.041	0.021 <sub>5</sub>	0.009
<i>1.3-ton Ingot.</i>									
<i>T1</i>	0.038	0.027	0.490	0.062	0.007	0.027	0.032	0.044	0.010 <sub>5</sub>
<i>T2</i>	0.031	0.022	0.459	0.047	0.006	0.028	0.029	0.020 <sub>5</sub>	0.008 <sub>5</sub>
<i>T3</i>	0.056	0.039	0.484	0.073	0.008	0.034	0.044	...†	...†
<i>T4</i>	0.061	0.050	0.490	0.079	0.008	0.033	0.045	...†	...†
<i>M1</i>	0.038	0.028	0.497	0.059	0.007	0.030	0.035	0.041 <sub>5</sub>	0.010 <sub>5</sub>
<i>M2</i>	0.036	0.025	0.473	0.052	0.006	0.031	0.033	0.022	0.008 <sub>5</sub>
<i>M3</i>	0.051	0.039	0.473	0.055	0.008	0.037	0.042	...†	...†
<i>M4</i>	0.063	0.048	0.484	0.075	0.008	0.039	0.044	0.021	0.012 <sub>5</sub>
<i>B1</i>	0.041	0.028	0.504	0.070	0.007	0.036	0.034	0.042	0.010
<i>B2</i>	0.038	0.025	0.480	0.064	0.007	0.037	...*	0.028 <sub>5</sub>	0.009 <sub>5</sub>
<i>B3</i>	0.053	0.036	0.480	0.076	0.009	0.038	...*	0.032	0.011 <sub>5</sub>
<i>B4</i>	0.045	0.036	0.470	0.065	0.007	0.036	...*	0.031 <sub>5</sub>	0.011

\* No sample available.

† These samples were too badly contaminated with blow-holes and oxide to justify melting them.

One bar from the middle of the ingot length, designated "middle"; one bar midway between the middle and top, referred to throughout as "top"; and one bar midway between the middle and bottom, referred to throughout as "bottom." In what follows, references to samples from "top," "middle" or "bottom" should be taken, unless otherwise indicated, as referring to the positions just defined.

As a result of the previous work on rimmed-steel ingots, it was considered that, instead of analysing the ingots at the Committee's standard positions and the sample strips in steps of  $\frac{1}{32}$  in. as had been done in previous cases, sufficient information would be forthcoming by making analyses at the following points on each strip :

- (1) Outer edge of the rim ;
- (2) inner edge of the rim adjacent to the rim/core junction ;
- (3) inside the core adjacent to the junction ; and
- (4) inside the core at a position midway between the junction and the centre of the ingot.

The results of the analyses for the three strips at these four positions from each individual ingot are shown in Table II. The figures for nitrogen and oxygen were obtained by the vacuum fusion method.

Figures 7, 8, 9 and 10 show the sulphur print and macro-etch of each of the strips actually used for analysis.

It has already been indicated that the procedure adopted in making and examining these particular ingots was directed towards elucidating the effect of mould size on the rimming process and product. In considering the data presented, it is proposed to discuss primarily this aspect of the matter, looking first at the general character of the ingots obtained, and, later, at a more detailed description of the heterogeneity disclosed.

### *General Characteristics.*

It is desirable perhaps, at this point, to make it clear that the control of the rimming action in the moulds by aluminium was not directed to obtaining a uniform type of ingot, but to maintaining a uniform addition throughout, in order that the results produced by varying ingot size might be strictly comparable. It was not to be expected, therefore, that all the ingots obtained would be typical ones. The actual aluminium addition made to control the rimming action (1 oz. per ton of steel) has provided an interesting series of ingot types, of which perhaps only the 2-ton ingot can be regarded as approximating to normal. If a different quantity of aluminium per ton had been used, different results would, of course, have been obtained in the various ingot sizes.

All four ingots present, with interesting variations, the well-known characteristics of rimmed material, *viz.* :

- (a) The marked difference between rim and core ;
- (b) the lenticular blow-holes found in the lower part of the rim ;
- (c) the presence of blow-holes at the junction of rim and core ;
- (d) the relative heterogeneity of the core part ; and
- (e) the existence of the so-called " cap " at the ingot top.

It is now proposed to discuss these characteristics in some comparative detail.

It is, of course, well-known that the thickness of the rim on rimmed ingots decreases with increasing carbon content of the material. The sections under review show that the rim thickness, with a constant carbon content, varies with the ingot size. Table III. shows the

TABLE III.—*Rim/Core Areas.*

Ingot Weight, Tons.	Position.	Thickness of Rim. In.	Ratio of Area of Rim to Core.
4.35	Top	4.3	1.55
	Middle	4.4	1.56
	Bottom	4.6	1.59
3.10	Top	4.0	1.71
	Middle	4.1	1.72
	Bottom	4.3	1.73
2.35	Top	3.7	1.84
	Middle	3.8	1.88
	Bottom	3.9	1.84
1.30	Top.	2.7	2.22
	Middle	2.9	2.24
	Bottom	3.2	2.57

actual thickness of the rim at the top, middle and bottom position of each ingot ; the rim increases gradually in thickness from the top to the bottom of the ingot in each case. Table III. also shows the ratio of the area of the rim to the area of the core on the three cross-sections. These figures disclose the interesting fact that the relative amount of rim to core decreases with increasing ingot size, and, further, that (apart from the bottom section of the smallest ingot, where accurate ascertainment of the junction was a matter of some difficulty) this ratio is practically constant throughout the ingot length.

The discovery of the fundamental factors which determine this ratio is of considerable importance, and the particular case under review would merit further study. It seems probable, from a preliminary survey, that the variation in the rim/core ratio with a constant carbon content is associated with the relationship between the periphery and the mould cross-section. This, in its turn,

suggests that the form of the moulds (square, rectangle, circle, &c.) would also affect the ratio under otherwise constant conditions. It is unlikely, however, that geometric relationships alone are the only factors involved; mould thickness, temperature and time may all play a part.

The lenticular blow-holes shown by the four sections are found in the normal positions, *i.e.*, along the base of the ingot, and in the rim itself throughout a part of the ingot length. It is hoped to show later that the depth below the surface and the height through which they persist from the bottom of the ingot have a significance and are related also to the ingot size. Meantime, it may be noted that measurement shows the positions occupied by these to be as follows :

Ingot weight. Tons . . . .	4	3	2	1
Height of blow-holes in rim. In. . .	29½	31	27½	36
Depth under surface. In. . . .	2-3	1½-3	1½-2½	2¼-3¼

In all cases the thickness of sound material separating these blow-holes from the ingot surface is sufficient to ensure good surfaces on rolling. It is only in cases of weakly effervescing metal that these holes approach the surface in a harmful manner, and this difficulty should not arise in making rimming steel when the effervescence is adequate and controllable.

The character and distribution of the blow-holes at the rim/core junction vary somewhat. In the three larger ingots these holes are of considerable size and irregular form along the bottom of the ingot and for approximately one-third of the ingot length. In the middle part of the ingot length in each case they tend to diminish in numbers, but again increase numerically, although of smaller size, in the upper portions. In the smallest ingot, in the lower part there is an irregular distribution of blow-holes throughout the core, and their distribution does not assist in defining the rim/core junction. In the upper part of the ingot, the junction blow-holes follow the distribution and form found in the larger ingots.

In the 1-ton ingot, in addition to the irregular blow-holes in the lower part already mentioned, there are a few larger blow-holes towards the centre, and these become very numerous towards the top of the core. In the 2-ton ingot there is a considerable number of large irregular blow-holes in the top third of the ingot, whilst a smaller occurrence of large blow-holes is to be noted in the top portion of the 3- and 4-ton ingots.

Whilst the chemical heterogeneity of the ingot, as a whole, will be considered later, the outstanding features of the core heterogeneity may conveniently be noted here.

The heterogeneity defined by sulphur-printing varies considerably from ingot to ingot. In the 1-ton ingot there is some slight  $\Lambda$ -segregate. This type of segregate is also very evident towards the top of the 2-ton ingot. In the 3-ton ingot it is less marked,



but again becomes very evident in the 4-ton ingot. V-segregate is in evidence around the axis of all three larger ingots, but becomes very marked in the upper portions of the two largest ingots.

In general terms, there would appear to be a larger proportion of reasonably homogeneous material in the core in the 2-ton ingot than in any of the others, although the lower portions of the 3- and 4-ton ingots are very clean and uniform for material of the kind.

One further feature of the core heterogeneity falls to be specially noted. In the 3- and 4-ton ingots, there is a pronounced V-shaped segregate at the very top, similar in form to the major segregation found in killed-steel ingots. This is absent in the two smaller ingots, although in the 2-ton ingot there is a small patch of slag with a relatively heterogeneous saucer-shaped layer of material around it.

The tops of all four ingots present an interesting study. Their general appearance is reproduced in Fig. 2. The 1-ton sample shows an irregular cauliflower top, obviously the result of eruption; the 2-ton ingot has a slightly sunken top with one small point of eruption; the 3-ton ingot has an almost flat top, except towards the centre, which has sunk slightly with one point of eruption; whilst the 4-ton ingot shows a smooth sunken top.

The cross-sections of these tops as shown in the sulphur- and macro-prints (Figs. 3, 4, 5 and 6) throw a considerable light on their formation. In the 1-ton ingot the formation of the "cap" of pure material, similar to and in continuation of the rim, appears to have proceeded normally until the still liquid or pasty core portion erupted through what was left of the top opening, subsequently solidifying and sealing off the whole core. In the 2- and 3-ton ingots, the cap formed apparently as an extension of the rim and is appreciably thicker in the 3-ton section. Following the formation of the cap, or when the remaining orifice was of very small dimensions, internal gas pressure blew up the small knob shown in the photographs and sections. It is of interest that in both these cases the core of the ingot appears to have subsided somewhat, following the formation of the rim/cap extension. Finally, in the 4-ton ingot, the thickest cap of all has been formed, but there is no evidence of the subsidence of the core portion just noted.

### *Chemical Composition.*

It is now necessary to consider the chemical heterogeneity revealed by the analyses, given in Table II., at the four selected positions in the three horizontal planes.

It is a matter of some difficulty to present these adequately, as the number of results is too large for comparison by inspection but too small for graphical representation. A series of tables was prepared, suitably arranged, to permit of easy comparison in con-

sidering particular aspects of the variations, and, from these, short descriptive summaries have been drawn up. It is proposed here to give only the summaries.

Three particular comparisons appear to be important :

- (a) Horizontal variations in composition at different heights;
- (b) vertical variations; and
- (c) variations related to ingot size.

(a) *Horizontal Variations.*

The variation in composition across the ingot width has been studied now in a considerable number of cases, and the published work all shows certain well-defined changes in composition from the outside of the rim to the centre of the core.

Generally, there is, in the case of phosphorus, sulphur, manganese, carbon, oxygen and nitrogen, a fall in the amount present across the rim, followed, in some ingots and for some elements, by a sharp peak on the core side of the rim/core junction. Thereafter the core composition from this peak to the centre is more or less uniform (apart from local irregularities), the amount of the various elements present being usually somewhat higher than in the rim part. This, of course, is not invariably the case, as, for instance, in ingots of "balanced" composition or less, when the carbon of the core is stated to be lower than that of the rim. Similar effects are frequently encountered also with oxygen and manganese.

The general form of any graph depicting variations in composition across the ingot is, however, quite characteristic : A fall in the rim, a discontinuity at the junction of the rim and core, followed by a more or less straight line across the core.

The four points from which the analyses of the present ingots were taken give results which conform to this general pattern.

The phosphorus and sulphur, which, in general, follow each other, are shown to be some 80-90% of the pit-analysis figure at the extreme outside of the rim, and fall to 60-80% of the pit figure at the inside of the rim. The amount present at this point is invariably the lowest found in any position for any particular plane. Both elements show a peak figure on the core side of the junction, but the degree of segregation varies from 60 to 70% over the pit analysis for phosphorus and from 68 to 85% for sulphur, except in the bottom positions of the three larger ingots, and in all positions of the 1-ton sample, where the variation from the pit figure is not so great. The top and middle sections show lower figures midway between the junction and the central axis. These figures vary some 40-60% over the pit figure. The bottom portion, and again the smallest ingot throughout, show smaller variations.

Although only one point between the junction and the centre of the ingot has been taken for analysis, it seems safe to assume

that, apart from accidental local concentrations, this figure represents the average composition of the core excluding the junction peak.

The manganese figure at the outside of the rim is the same as or only 1–3% in excess of the pit figure. It falls throughout the rim until it is anything down to 15% below the pit analysis. There is no definite indication of a peak at the junction, and the core figures in both positions fluctuate approximately  $\pm 4\%$  from the pit figure.

The carbon results on the outside of the rim are, with one exception, over the pit percentages, and they show considerable fluctuation. This may be due, in part, to contamination by mould wash (tar was used). The figures at the inside of the rim show the usual fall, all the results (with one exception) being considerably below the pit figures. The carbon content at this point is also the lowest at any of the positions examined for each particular plane. At the junction the carbon rises sharply and there is, in some cases, a suggestion of a peak, as the figure at the mid-core point is lower than that at the junction. Throughout the core the carbon is above the pit analysis and considerably in excess of the rim composition figure, although the actual excess varies greatly from plane to plane and from ingot to ingot. If the Hultgren and Phragmén<sup>1</sup> balanced composition hypothesis is correct, it would seem that their suggested figure of 0.06% of carbon is too high.

The oxygen content falls from a maximum at the surface of the rim but rises again in the core, subject to local variations throughout the length, to be described later.

The nitrogen content of the rim is relatively low—about 77% of the pit figure—and falls at the rim side of the junction still further. Throughout the core it rises, except in the bottom position, to about the pit content of 0.013%.

### (b) *Vertical Variations.*

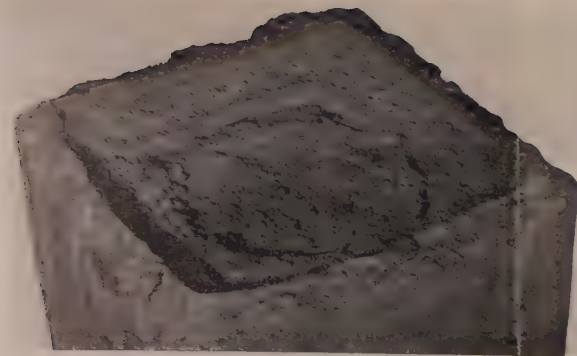
The trend (in some cases it is little more than an indication) of the variations in a vertical direction are frequently suggestive.

Phosphorus in the outer rim samples tends to fall from the bottom to the top of the ingot. This is still more marked in the figures for the rim material adjacent to the junction. In the core samples this is reversed, and the phosphorus rises from bottom to top. The trend is not so clearly marked in the core sample at the junction as in that taken midway towards the centre, but the reversal of direction is quite apparent. The bottom core samples in all the ingots are at most 20% above the pit figure, as compared with 50–80% for the higher positions, except in the small ingot, where the figures are still lower.

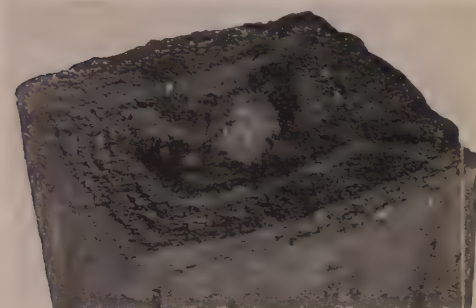
The sulphur in the rim has the same trend as the phosphorus, *i.e.*, it tends to fall towards the top. The core proper again shows increasing sulphur towards the top, but the core sample at the

<sup>1</sup> *Jernkontorets Annaler*, 1938, vol. 122, No. 8, p. 377.

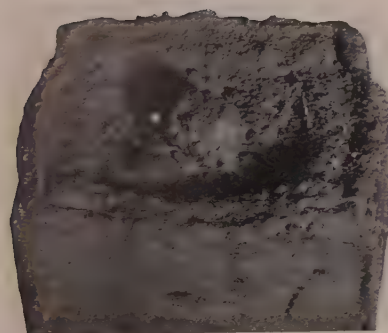




(a) 4 Ton 7 cwt. Ingot.



(b) 3 Ton 2 cwt. Ingot.



(c) 2 Ton 7 cwt. Ingot.

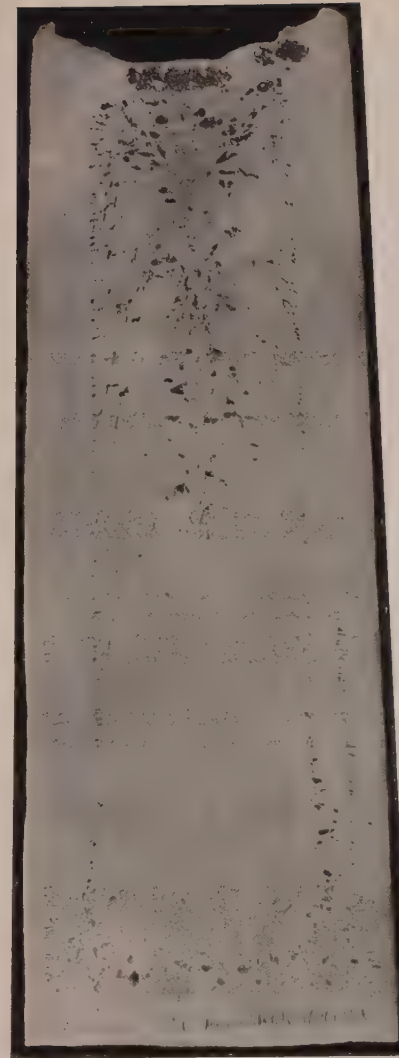


(d) 1 Ton 6 cwt. Ingot.

FIG. 2.—Tops of the Ingots.

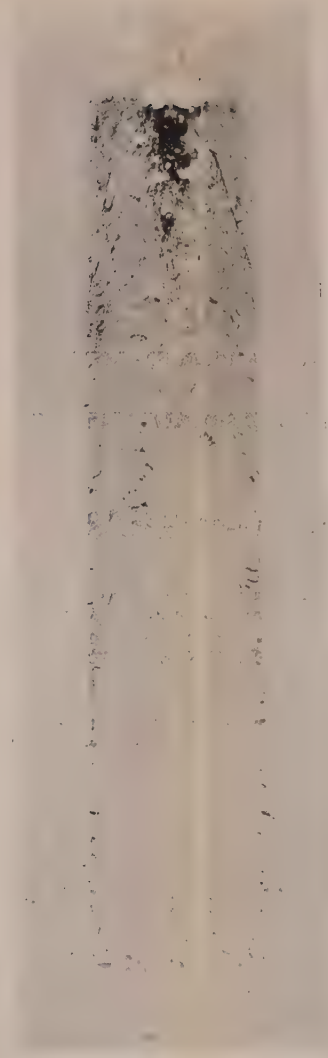


(a) Sulphur Print.

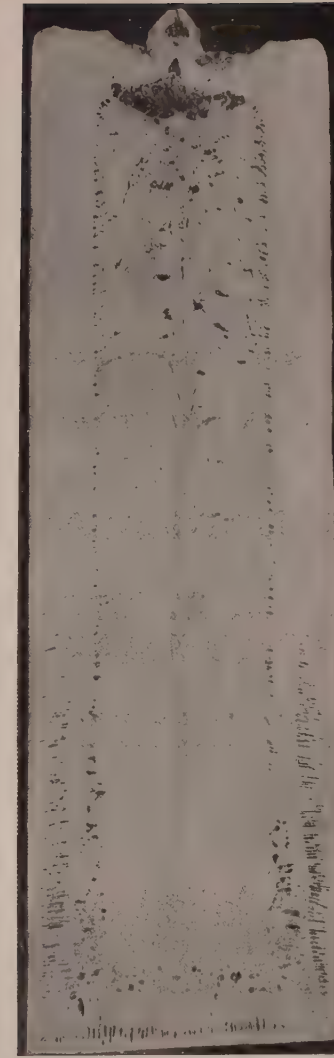


(b) Macro-Etching.

FIG. 3.—4-35-Ton Ingot.

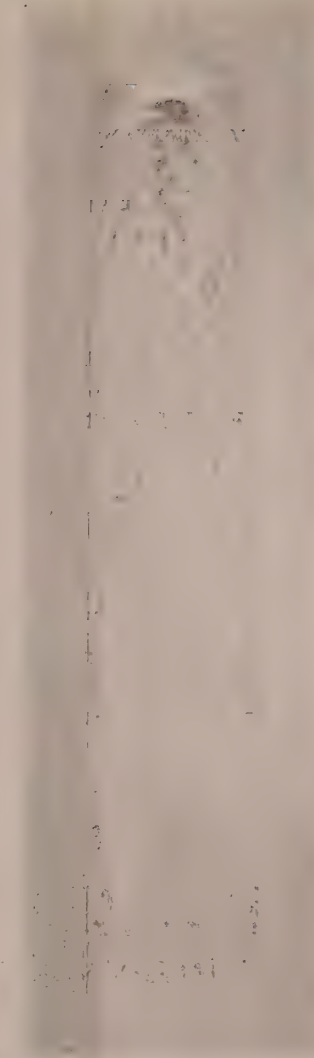


(a) Sulphur Print.

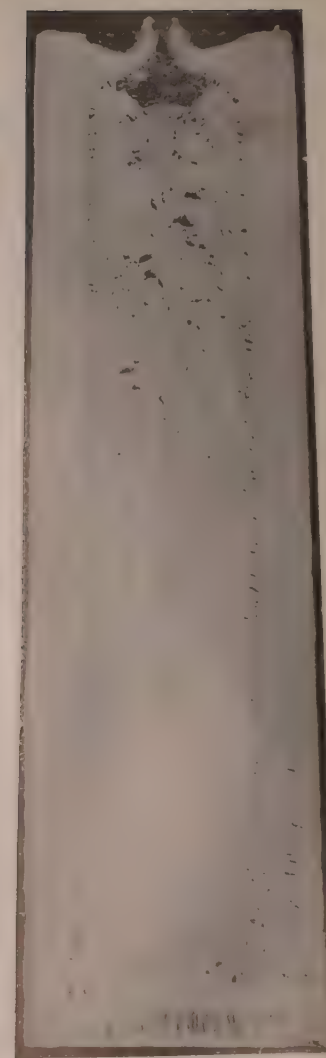


(b) Macro-Etching.

FIG. 4.—3-1-Ton Ingot.



(a) Sulphur Print.

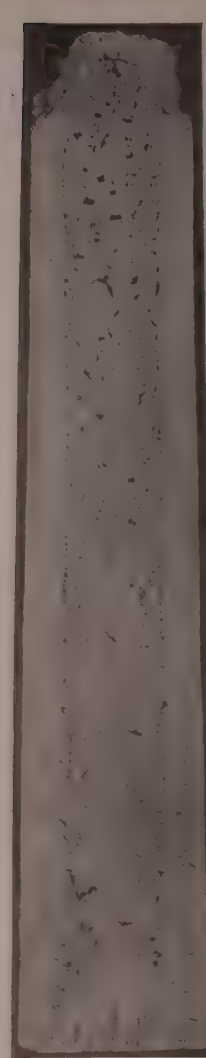


(b) Macro-Etching.

FIG. 5.—2-35-Ton Ingot.



(a) Sulphur Print.

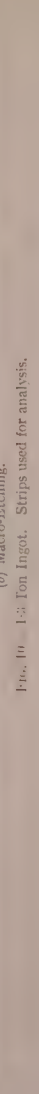
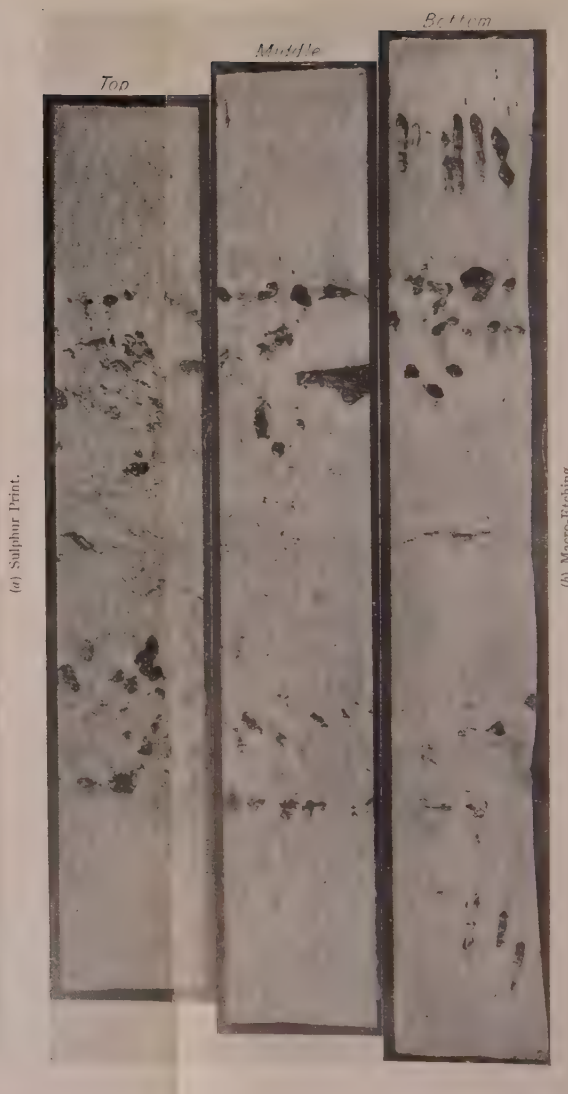
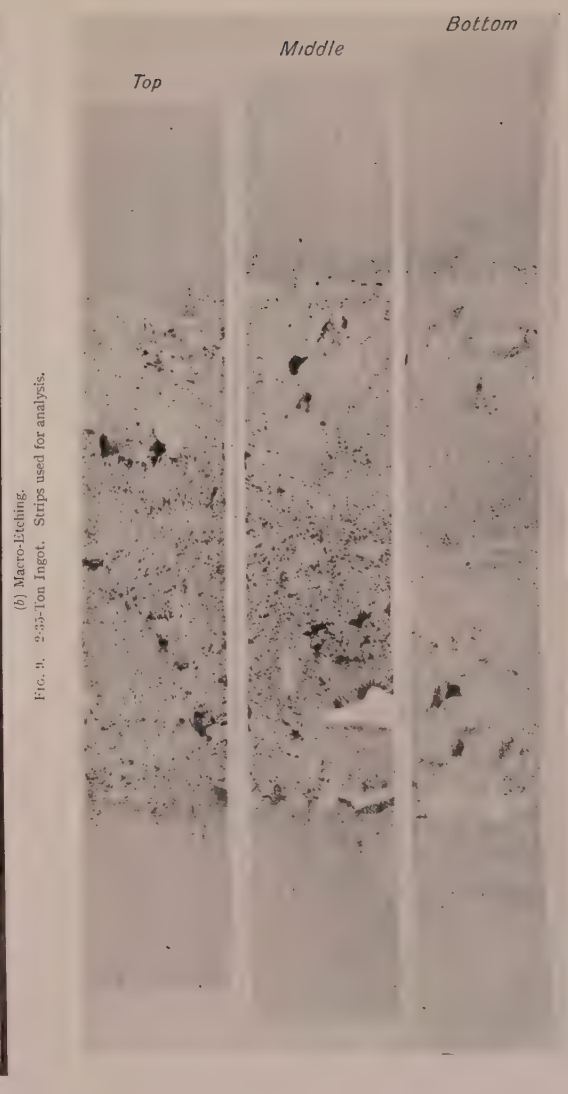
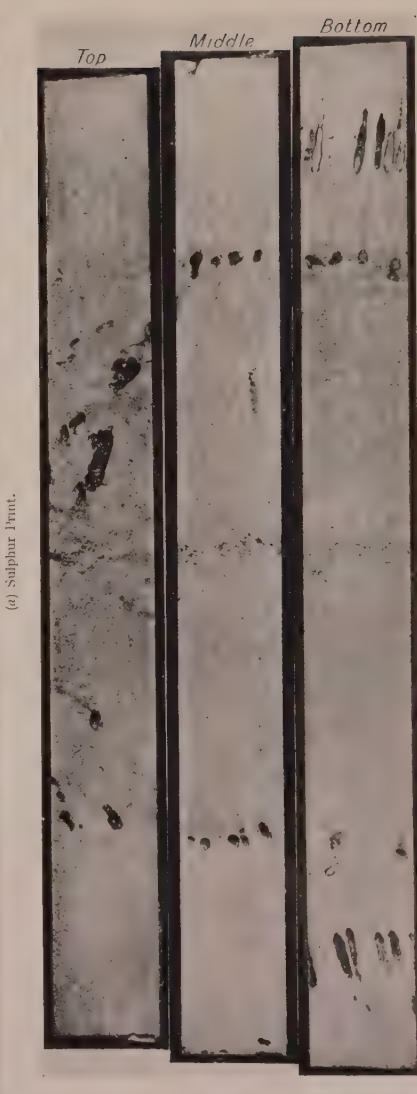
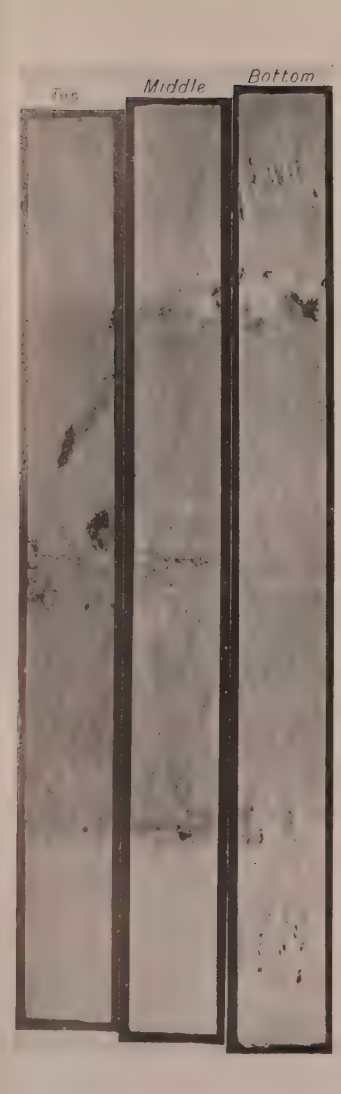
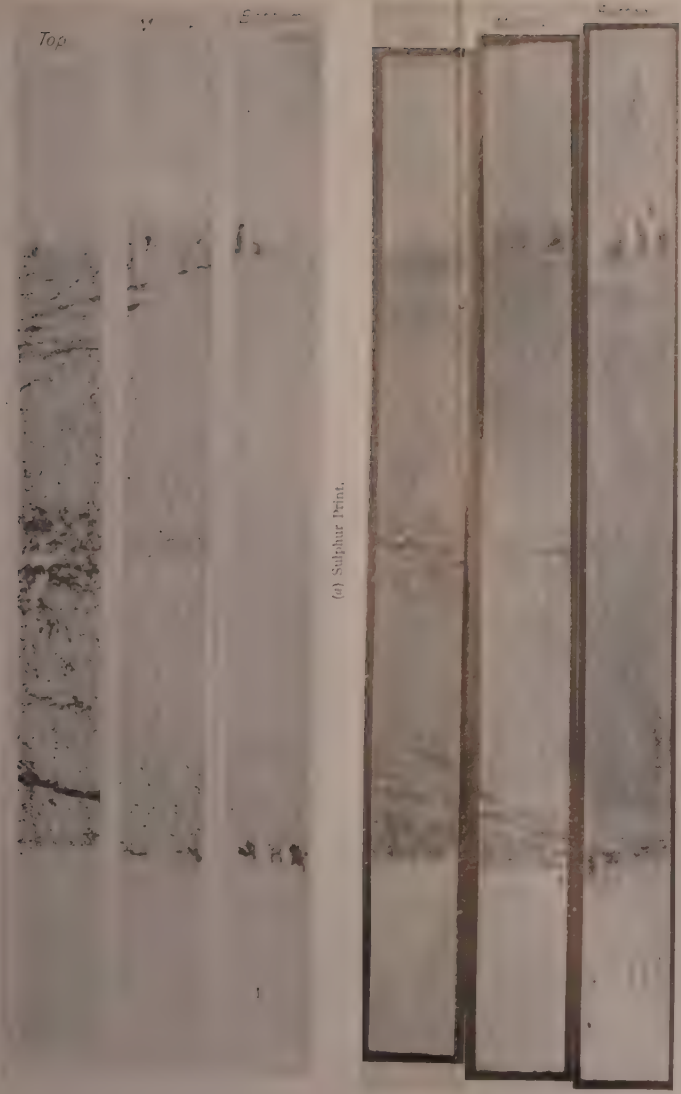


(b) Macro-Etching.

FIG. 6.—1-3-Ton Ingot.

(Mitchell,  
To face p. 356.)







junction is highest in the middle position. The top, however, is still above the bottom in sulphur content. The excess of sulphur present, relative to the pit analysis, is of the same order as for phosphorus.

The bottom strip for all ingots shows that, so far as phosphorus and sulphur are concerned, the material in that position contains little more segregation than might be expected in some killed steels, although the metal is, of course, quite different as regards texture.

Manganese also appears to fall slightly in both rim positions towards the top of the ingot, whilst the core variation, although small, is in the reverse direction.

The carbon variations in the rim and core follow the same direction as the other elements, although the outer rim figures are not conclusive, probably because of the mould wash contamination already mentioned.

In the case of oxygen, the inner rim figure definitely falls from bottom to top, but the outer rim is without even the suggestion of a definite trend. In the core, although the general direction is not very marked, the top is somewhat higher in oxygen than the bottom.

Nitrogen would appear to be lower in the bottom of the core than at the middle or top, but, apart from this, there is no variation calling for particular comment.

It will be seen from this summary that there appears to be a well-defined tendency for the segregating elements to diminish in the rim and to increase in the core from bottom to top of the ingot. For the particular bottom position chosen for sampling, *i.e.*, one-quarter of the ingot length from the bottom, the metal approximates much more closely, in the core, to the average or pit composition than might be expected from the appearance of the sulphur-macro-prints.

#### (c) *Variation in Composition with Ingot Size.*

There is a distinct indication that increasing ingot size is accompanied by greater purity in the rim. This is particularly noticeable in the sulphur figures, but can be seen by comparing the percentage of any of the other elements recorded in the analyses (except, perhaps, nitrogen) at any of the horizontal positions—top, middle or bottom.

A careful examination of the composition of the core fails to reveal any trend which can be attributed to ingot size. It does show, however, that the 1-ton ingot under examination differs in a very marked way from the other three in the degree of segregation related to pit analysis in the core, at various positions. Table IV. shows this, the numbers used being based on a pit analysis of 100. The degree of carbon segregation at the bottom is greater than in the larger ingots, whilst the degree of segregation of the other elements is generally less, particularly in the middle and top positions.

TABLE IV.—*Comparison of Degree of Segregation in Core.*

Pit analysis = 100.

Sample 3 = core side of rim/core junction. Sample 4 = midway between junction and centre.

Position and Sample No.	Phosphorus.		Sulphur.		Manganese.		Carbon.	
	Average 2-, 3-, 4-ton Ingots.	1-ton Ingot.	Average 2-, 3-, 4-ton Ingots.	1-ton Ingot.	Average 2-, 3-, 4-ton Ingots.	1-ton Ingot.	Average 2-, 3-, 4-ton Ingots.	1-ton Ingot.
Top 3 . .	162	122	173	122	103	101	158	138
4 . .	163	132	169	132	102	96	157	149
Middle 3 . .	163	110	186	125	101	96	148	104
4 . .	140	137	153	155	100	98	128	141
Bottom 3 . .	114	115	117	116	93	98	109	143
4 . .	112	98	118	116	92	96	111	122

It is, of course, natural that, if the rim is less pure in the small ingot, there would be much less marked segregation in the core, but it is peculiar that there should be such marked differences in this ingot only and that the others should not show at least some trend, related to their size, in the same direction. The contrast may be associated with the relatively large step in cross-sectional area between this particular ingot and the next in the series, or, alternatively, with the boiling-up action which preceded solidification in this particular case.

#### *General Discussion.*

It is considered that this study has provided some interesting pointers on matters relating to the practice in making rimming steel and to the not inconsiderable discussion on the theory of the process.

It would perhaps be desirable, at this point, to set out briefly the author's view as to what happens in the mould during the filling and solidification of a rimmed-steel ingot.

Ignoring chemical reaction for the moment, the physical effects which contribute to the sequence of changes that result in a rimmed ingot are mechanical turbulence and effervescence, and falling temperature with its accompanying solidification of molten material. The peculiar type of heterogeneity found in such ingots is the product of these two agencies.

The mechanical turbulence arises from three sources, of which possibly two only are operative at any one stage of the process. During filling, there is a considerable churning of the metal due to the action of the ladle stream. This is more marked in top-poured than in bottom-run ingots. There is the finer mechanical turbulence

arising from the effervescence following the chemical reaction  $\text{FeO} + \text{C} \rightarrow \text{CO} + \text{Fe}$ . After teeming has ceased, the second of these reactions continues, and the first is replaced by convection currents due to temperature differences. At all stages of the process, therefore, until the metal is solid there will be two distinct agitations : One arising from the effervescence proper, and the other from what might be termed the major circulation currents of the liquid material. The author accepts the view that, in general, the results of these disturbances are an upward movement on the freezing wall and a downward movement around the axis of the ingot.

It is not proposed to consider further the turbulence arising from teeming, but the mechanical movements which follow from convection currents and from chemical reaction are of great importance, and their influence persists until the whole mass of the material is solid.

In moulds of similar cross-sectional form, it seems reasonable to assume that convection currents will result in currents in the same direction irrespective of mould size, at least within fairly wide limits.

So far as the mechanical agitation due to effervescence is concerned, the degree of vigour of this reaction will depend on temperature, pressure at any point, and on the concentration of oxides and carbon. The duration of the reaction is also of primary importance. It should continue right up to the last possible moment at which the metal is still in a physical condition to permit of the escape of gas.

Apart from its effect on the gas-evolution reaction, the fall in temperature would appear to be important in two directions : The rate at which the metal is losing heat will determine the speed with which any one layer of metal is deposited on that immediately preceding it, and it will also determine the time available within which the gas-evolution reaction may continue, assuming that there are still sufficient reactants present for its continuance.

The solidification of the molten material, as regards composition, quantity and position, is the resultant effect of the two factors already mentioned, *i.e.*, mechanical action and temperature.

At the beginning of the process, just after the mould is filled, the first chilled layers are formed, the thickness of these depending largely on the immediate chilling action of the mould itself. It is, of course, only when the metal is too hot and the rate of formation of this shell too slow, thus giving time for the commencement of the gas-evolution reaction, that an immediate rise in the metal is to be expected. The rising metal, owing to a too-weak effervescence, is possibly a separate phenomenon and takes place at a slightly later stage. The cause of the rise in both cases is, of course, entrainment of gas bubbles in the surface layers. When conditions are correct, *i.e.*, when the temperature is right and the evolution of gas commences almost immediately the chill-layer skin is formed, no appreciable gas is trapped at this time.

Hultgren and Phragmén suggest that in steels below a certain carbon content the outer shell is formed by rimming rather than by a chilled action. They distinguish between a “rimmed skin” and a “chilled skin.”

In the author's opinion, a chilled skin is formed in steels of all compositions. The actual thickness of this skin will depend on the temperature of the metal, the mould temperature and probably the rate of filling, and its form and character represent straightforward solidification during the short interval of time before the carbon monoxide evolution commences. The commencement of this evolution will depend on the time taken to achieve a concentration of oxide on the cooling face sufficient to upset equilibrium and commence the gas-evolution reaction.

If this view is correct, it would be expected that the solid envelope at the bottom of the ingot would not vary with the ingot size for the same metal, assuming that the moulds were of equal thickness and at the same temperature. This is supported by the figures on p. 333 P showing the depths under the skin at which the lenticular blow-holes are found.

The concentration of oxide in the metal next to the freezing layer arises, as suggested by McCance, from the low solubility of FeO in solid iron. As  $\delta$ -iron is precipitated to form the rim, the rate of enrichment of the mother-liquor with oxide will depend on the rate of rim formation, and the vigour of the effervescence will, therefore, be affected. The more quickly the rim forms, the sooner will the effervescence be built up to a maximum. This means that, with smaller ingots, one would expect a more violent agitation at this stage and that, therefore, other things being equal, more aluminium would be required to keep the movement due to gas evolution within reasonable bounds. It follows that, for the same metal, more aluminium will be required with small than with large ingots, as will be seen later. The present series of ingots supports this line of reasoning, as does practical experience generally. Once effervescence is well established, the upward sweep of the gas bubbles and currents in the molten metal arising therefrom play a major part in the character, both physical and chemical, of the rim which will be obtained.

It is necessary, however, to examine more closely the mechanism of rim formation. The author suggests that the solid rim is the result of two distinct processes :

- (a) Solidification of some liquor of average composition *in situ* due to local temperature, *i.e.*, normal crystallisation of material from the mother-liquor, and
- (b) The deposition of iron particles of high relative purity which are the product of the iron-oxide/carbon reaction.

The second of these is analogous to “the coming to nature” of the puddling process, and is indeed the same reaction, both chemically



and physically, but taking place under slightly different physical conditions, more particularly as regards temperature.

It may be considered, in view of the comparatively small amounts of oxygen and carbon involved in the reaction, that the quantity of iron arising from this source is too small to affect the process appreciably. The actual iron particles arising from the reaction, however, will no doubt serve as nuclei and carry down with them considerably more iron than is represented by their own initial weight. The rim of the ingot can be regarded, therefore, as being made up of relatively impure crystals which have solidified in the usual way, and precipitated grains or crystals of very pure iron, having their origin in the gas-evolution reaction. Under the conditions prevailing, these two components will weld to form a continuous crystal mass.

The significance of this conception in relation to many obscure phenomena associated with rimmed ingots, such as lenticular blow-holes and cap formation, will be discussed later.

The combined movement in the metal, due to effervescence and to temperature gradients, ensures circulation of the liquid core, and, generally, induces an upward movement and coalescence of non-metallic particles. So long as the gas reaction continues, the rim will continue to grow and the remaining mother-liquor will become more and more impure.

The whole process is finally arrested for one of two reasons: The impure mother-liquor reaches its freezing range, and, if the reaction is still vigorous, its suppression will be accompanied by a more or less violent eruption of the pasty mass, as seen in the 1-ton ingot, Fig. 6. Alternatively, the gas reaction may be suppressed by increased pressure, *e.g.*, when the top cap freezes over or when, as is often done in practice, the top is capped by a plate. A special case to be noted is that in which the gas reaction is suppressed in the manner just suggested or dies away because of a shortage of reactants (in this case oxide) and a liquid impure core is left to freeze without any major agitation. This leads to segregation effects similar to those obtained in the cooling of killed steel, the rim, already formed, acting as a mould and the whole system being under conditions representing solidification under very slow cooling. This would explain the major V-segregation and streamer segregates shown in the 3- and 4-ton ingot sections in Figs. 3 and 4.

Before proceeding to discuss, in the light of these suggestions, the specific case of the four ingots under consideration, it might be well to look briefly at the interpretation that they put on two of the characteristics of rimmed ingots which have provided material for very considerable discussion: The top cap or crust, and lenticular blow-holes.

The author regards the top cap as an extension of the rim and considers that it is formed by the same combination of ordinary crystallisation and precipitation as the rim itself, the latter action



predominating. The way in which the cap thins off towards the liquid centre (to be noted particularly in Fig. 6) shows that it is formed chiefly by an aggregation of precipitated particles rather than by the normal processes of freezing-out from a liquid mass. Where the cap achieves considerable thickness, this is an indication of the time of ebullition, although it is possible that the original precipitated base will act as a foundation from which ordinary crystal growth can take place, provided that the liquid material does not subside owing to shrinkage from other causes in the meantime. If the initial layers result in a concave crust, as in the case of the 4-ton ingot (Fig. 3), conditions will favour the formation of a relatively thick cap, owing to the prolonged contact between the solid metal and the liquid core. Where a cavity is formed, the crust will not grow to the same thickness, and the accumulation of gas in the cavity can ultimately cause a blow-out, as shown in Figs. 4 and 5. In any case, the crust will be continuous only if the metal remains molten long enough to provide sufficient material in one of the ways already suggested.

Turning to the lenticular blow-holes, it is now generally agreed that these are due to entrapped gas produced by the oxide-carbon reaction. The question of the formation of the outer section which separates these holes from the ingot surface has already been mentioned, and it seems possible that their longitudinal form arises from the inward growth of the dendrites. What is not so readily explicable is the abrupt manner in which these holes stop. Almost invariably, the inner end of the holes is marked by a clearly defined line in an upward direction. It has been suggested that this represents the point in the process at which the upward sweep of the mould gases becomes effective in preventing the lodgement of further gas. This seems unlikely, in that the conditions become less favourable for this sweeping action as the mould area becomes more constricted. If this were the only explanation, one would also expect to find the lenticular blow-holes in ingots of small cross-section persisting to a greater degree than those in ingots of large cross-section. The present series of ingots shows that this is not so.

It has also been suggested that the relatively high pressure at the bottom of the ingot may have caused a cessation of the gas reaction and there is, in fact, no gas being evolved in the particular zone in which these are found. The fact that the height to which these holes persist in these four ingots, which are of approximately the same length, varies with ingot size, casts some doubt on the correctness of this hypothesis. The figures for height given on p. 333 P show that, in general, the lenticular blow-holes are found to be higher in the ingot the smaller the ingot size. This gives some support to the washing action but none to the pressure theory. It seems probable that the real explanation is that the solid rim on the inside of these holes is largely due to the precipitation mechanism already outlined and that the holes themselves stop abruptly at the

point at which the primary dendritic crystallisation is replaced by equi-axed crystals following precipitation.

The conception of the general rimming process given above would appear to fit in with the observed differences in the four ingots under discussion.

Returning for the moment to the particular blow and its nature, there is abundant evidence that both the temperature and the degree of effervescence (two guides by which an operator can achieve any required type of ingot) were satisfactory. The temperature was adequate. It was possible to stand 4 min. before teeming without producing a ladle skull and to disseminate uniformly throughout the metal the manganese from the ferro-manganese additions. The effervescence was vigorous during casting, a condition not attainable if the metal is too hot. That the effervescence was satisfactory is shown by the fact that not one of the ingots "rose" during or immediately after filling. The depth of the lenticular blow-holes in the rim below the surface confirms this conclusion. That the degree of effervescence was not excessive is indicated by the absence of any sign of "boot-legging." The initial state of the converter material provided the margin necessary to permit of control by aluminium. This control has a two-fold purpose: It regulates the vigour of the effervescence and determines its duration. The use made of each or either of these in practice depends on the time when the aluminium is added. In the author's opinion, in the case under review, *less* aluminium should have been added to the 3- and 4-ton ingots and rather *more* to the 1-ton sample; the addition made was correct for the 2-ton ingot. This opinion is based on the belief that the duration of the effervescence was the critical factor in producing the differences exhibited by the various samples. In the 1-ton ingot, the gas reaction appears to have continued after the metal was in a "mushy" state, thus causing the eruption which produced the irregular head. With more of the available oxygen "fixed," this would not have happened. In the 3- and 4-ton ingots, the gas evolution appears to have died away before the core was at the solidification temperature; this left the still liquid core in a comparatively quiescent state standing in a mould of rim material in the manner described earlier. The obvious flotation of impurities in the major V-segregate at the top in each case followed. If mechanical agitation had continued, the relatively pure core in the lower part of the larger ingots and the relative impurity of the top part would not have been so pronounced.

It is now possible to suggest an explanation of some of the other differences noted in reviewing the results from these ingots. So far as heterogeneity was concerned, it was observed that the rim was relatively pure from bottom to top and that the core was relatively impure. Further, the relative purity of the rim increased as the ingot size increased. It is suggested that the relative proportion of precipitated pure material in the rim to crystallised

material accounts for these differences. Where the relative quantity of crystallised material is high, *i.e.*, where quick cooling has been taking place—for instance, at the base of all the ingots and in the upper part of the smaller ones—there will be less of the relatively pure material present, and, therefore, the average composition will be less pure. The well-known increase in purity inwards on the rim section at any point, confirmed in these ingots, can be explained in the same way. The chilled skin and the first layers to crystallise will crystallise in the normal way, but, as the gas reaction increases in intensity, increasing quantities of the pure precipitate will accompany these primary crystals in the rim itself. This does not detract from the importance of the washing action, which prevents the lodgement of gas and which also helps to distribute the precipitated iron crystals uniformly.

The relatively large proportion of rim to core in the smaller ingot follows, being due to the steeper temperature gradient; there will be more crystallisation and less precipitation, even in the upper parts. Conversely, in the larger ingots it is natural that one should find that the rim in the upper part is relatively more pure than in the smaller ingots.

#### *Conclusions.*

This investigation shows that moulds of different sizes require metal of varying degrees of effervescence to produce ingots of the same character, and that, in general, where extreme purity of the rim is desirable for practical purposes, this can be better attained in larger than in small ingots, provided that the initial material has a sufficiently vigorous effervescence to be controlled by aluminium.

Any ingot size, within the limits studied, is permissible, provided that the rimming characteristics of the metal are modified to suit the particular size of ingot selected, although it is probable that in day-to-day practice it would be easier to secure a better mill yield from smaller-sized ingots, other conditions being the same.

#### *Acknowledgments.*

In addition to the thanks due to Messrs. Stewarts and Lloyds, Ltd., for providing the ingots, the author would like to express his appreciation of the help received from Dr. T. Swinden and Dr. H. A. Dickie. The sulphur prints, macro-etch and vacuum fusion analyses were carried out by the Central Research Department, The United Steel Companies, Ltd., whilst the general analyses and various other necessary tests were carried out by Dr. Dickie and the staff of the Department of Research and Technical Development of Messrs. Stewarts and Lloyds, Ltd.

[This paper was discussed jointly with the two preceding papers by D. Binnie on "An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process," and by J. Mitchell on "Rimming Steel" and the two following by T. Swinden on "Rimming Steel" and by T. Swinden and W. W. Stevenson on "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C."]

# RIMMING STEEL.—ADDITIONAL STUDIES OF THE COMPOSITION VARIATION FROM OUTSIDE TO CENTRE.\*

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(Figs. 8 to 12 = Plates XXX. to XXXIII.)

*Paper No. 15/1942 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

This paper represents a continuation of the work reported in Section III. of the Ninth Report on the Heterogeneity of Steel Ingots, with particular reference to the Hultgren and Phragmén hypothesis on rimming action. It deals with a basic open-hearth steel ingot from a cast with a pit-sample carbon content of 0.047% and containing only 0.10% of manganese.

No essential difference in the type of inclusions was found as compared with rimming steel of more normal composition.

Variations in composition as regards carbon and oxygen (and also hydrogen and nitrogen) have been traced. The data thus obtained provide excellent verification of the hypothesis postulated by Hultgren and Phragmén, and the actual values of carbon and oxygen representing the balanced composition, namely, 0.06% carbon and 0.04% oxygen, appear to be substantially correct.

Two previous papers <sup>(1, 2)</sup> by the author have recorded data obtained in the examination of sections of rimming steel, together with observations on the theory of the rimming action in the light of contemporary researches on the subject. A good deal of attention was deservedly paid to the paper by Hultgren and Phragmén <sup>(3)</sup> of which a detailed exposition has been provided by Edwards <sup>(4)</sup> and Myers. <sup>(5)</sup> In the author's last paper, <sup>(2)</sup> a summary of the conclusions reached by Hultgren and Phragmén is given, in which the following statement appears :

As a consequence of the reaction :

Carbon (in solution) + oxygen (in solution)  $\longrightarrow$  CO (+CO<sub>2</sub>) (gas)

there exists a balanced composition characterised by the carbon and oxygen concentrations of the liquid remaining unaltered so long as gas is freely evolved during freezing. This composition is probably not far from 0.06% of carbon and 0.04%

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of oxygen, assuming the metal to be saturated with respect to the gas reaction. For metal with a higher carbon content, carbon will increase and oxygen decrease in the liquid metal during freezing under gas evolution; for metal of lower carbon content the opposite holds true.

Fig. 1 reproduces in graphical form the progressive variation of the carbon and oxygen contents in two freezing systems of rimming steel, the carbon contents of which are (a) above and (b) below the stipulated balanced composition. Thus in system (a), Hultgren

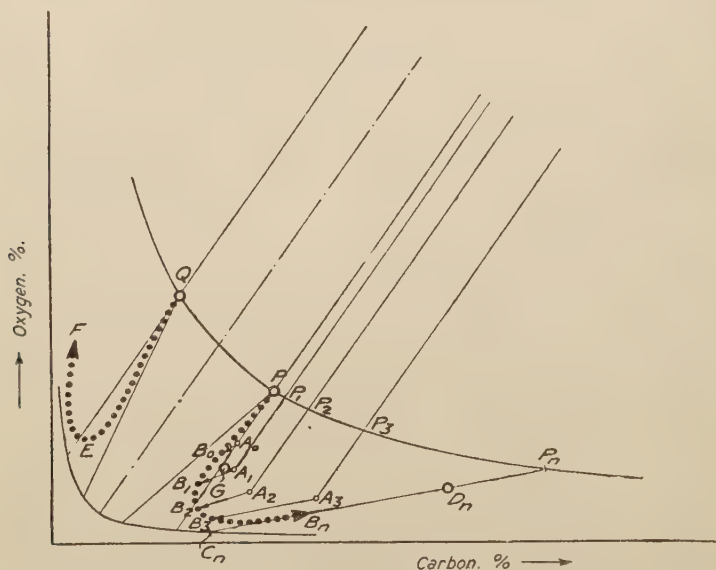


FIG. 1.—Diagrammatic Representation of the Influence of Gas Reactions, Undercooling and Stirring of the Liquid on the Composition of the Rim Zone (Hultgren and Phragmén<sup>(3)</sup>).

and Phragmén postulated that a liquid metal  $P$  would form a rim zone varying in carbon and oxygen contents along the curve  $P, B_0, B_1, B_2, B_3$ , the mass of metal remaining to form the centre of the ingot being a mixture of liquid  $P_n$  and crystals  $B_n$  having a mean composition  $D_n$ . In system (b), with a carbon content of the liquid metal below the balanced composition, the carbon and oxygen contents of the rim zone and into the core zone would progress along the curve  $QEF$ .

In Fig. 2 are reproduced the carbon-oxygen curves obtained on samples taken from the outside to the centre of a  $10\frac{1}{2}$ -in. square bloom of basic open-hearth rimming steel, cut from positions approximately one-third and two-thirds of the distance from the



bottom of the ingot. Full details of this examination are given in the Ninth Report of the Ingots Committee<sup>(2)</sup> and the results illustrate the composition to be expected from a steel having a carbon content higher than that of the balanced composition. The three pit samples from this cast, 34/8940, contained 0.10% of carbon, the rest of the analysis being manganese 0.31%, sulphur 0.044% and phosphorus 0.017%. It is seen from Fig. 2 that the general form of these curves is of the correct order for a steel of carbon content greater than 0.06% according to the hypothesis of Hultgren and Phragmén. The process of freezing is that carbon and oxygen decrease together to a certain depth, where the carbon reaches a minimum and starts to increase again, the oxygen still decreasing.

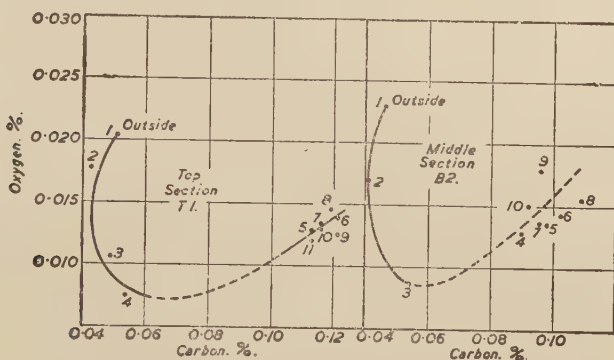


FIG. 2.—Basic Open-Hearth Rimming-Steel Ingot, Cast 34/8940. Ratio of total oxygen to carbon values. The numbers represent the positions from outside to centre of the ingot.

At still greater depth, the oxygen reaches a minimum and starts to increase somewhat. Quoting further from the author's last paper<sup>(2)</sup>:

It is unfortunate that we have no complete data to prove whether the variations in composition would, in fact, follow curve *QEF* in steel of appropriate carbon content.

Certain indications are then quoted which suggest that the course of curve *QEF* would probably be followed in rimming steels of very low carbon content. *Ample confirmation has now been obtained that the postulated form of curve QEF does, in fact, occur.* The two sets of data are not absolutely comparable; the earlier work quoted above was carried out on a 10½-in. square bloom rolled from a 22½-in. square ingot, the bloom section being deliberately chosen, in preference to an ingot section, to overcome the difficulty of obtaining satisfactory specimens for oxygen determination in the presence of ingot blow-holes. The present work has been

done on an ingot section of very low-carbon rimming steel, the selected ingot being comparatively free from internal blow-holes.

### CAST H3906—VERY LOW-CARBON RIMMING STEEL.

An ingot of this type was described very fully as Example 65 in the Sixth Report of the Ingot Committee.<sup>(6)</sup> Example 65 was unfortunately not available for further examination, but a similar ingot from cast H3906, a 75-ton cast of very low-carbon basic open-hearth steel made at Stocksbridge, has now been examined.

A pit sample taken alongside the ingot examined had the following analysis :

Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.	Oxygen.
0·047%	0·10%	Trace	0·017%	0·007%	0·039%

The cast was made a considerable time ago and the pit-sample oxygen was determined by the Herty method. Subsequent work has indicated that the Herty figures are indicative rather than absolute, and under the conditions of manufacture of this cast would tend to be on the low side.

The ingots from cast H3906 were top-poured, singly, through a 1-in. clay nozzle, and were cast in 45-cwt. moulds. Ingot No. 6 was selected for examination, and after sectioning longitudinally down the centre, the central face was sulphur-printed and macro-etched, as shown in Fig. 8. The ingot face was then drilled with a 1-in. drill at five positions  $A_1$ ,  $F_1$ ,  $C$ ,  $F_2$ ,  $A_2$ , representing the full width of the ingot across the *AFC* plane of the Ingot Committee standard positions. The analyses of these five samples, together with the cast analysis for comparison, are shown in Table I. Fig. 3 indicates the location of the positions on the ingot. The main

TABLE I.—*Analyses of Samples taken from Five Ingot Positions in Ingot No. 6, Cast H3906.*

Position.	Carbon. %.	Manganese. %.	Silicon. %.	Sulphur. %.	Phosphor- us. %.	Nitrogen. %.
$A_1$ . . .	0·032	0·08	0·008	0·011	0·007	0·0035
$F_1$ . . .	0·039	0·09	0·008	0·022	0·009	0·004
$C$ . . .	0·038	0·10	0·008	0·022	0·007	0·004
$F_2$ . . .	0·038	0·10	0·004	0·023	0·007	0·004
$A_2$ . . .	0·035	0·09	0·010	0·011	0·006	0·004
Cast analysis .	0·047	0·10	Trace	0·017	0·007	...

feature of these analyses lies in the carbon contents at the five positions; in all cases, the carbon figures are definitely lower than the cast analysis shown by the pit sample. This is referred to later.

### *Preparation of Ingot Section for Detailed Examination.*

After sulphur-printing, macro-etching and drilling at five positions across the plane *AFC*, as described above, a transverse V-shaped slice was cut from the centre of the top face of the half-ingot. This slice was machined to a 2 in.  $\times$  1 $\frac{3}{4}$ -in. section and measured 8 $\frac{1}{2}$  in. from outside to the longitudinal central plane of the ingot. The face of this 2-in. slice was parted at about  $\frac{1}{4}$ -in. thickness for metallurgical examination of the structure and inclusions and for hardness tests; a second slice,  $\frac{1}{2}$  in. in thickness, was taken and cut into 2 in.  $\times$   $\frac{1}{2}$  in.  $\times$   $\frac{1}{2}$ -in. pieces. Starting from the outside of the ingot, seventeen such pieces were obtained to the centre-line and these were utilised for the determination of oxygen by the vacuum fusion method and for carbon determination. Additional vacuum fusion determinations were carried out both by the total and by the fractional procedures, at selected positions in a third slice of the 2 in.  $\times$  1 $\frac{3}{4}$ -in. section. The precise location of the test-pieces is illustrated in Fig. 4.

### *Metallurgical Examination.*

(1) Photographs of the *sulphur print* and *macro-etched face* of the central slice cut from ingot No. 6 of cast H3906 are shown in Fig. 9. The sulphur print is that of a deeply rimmed steel, free from the normal heavy segregations at the junction of the rim and core and within the core. The macro-etching shows a fine equi-axed grain in the rim with very little evidence of columnar growth. A number of very small blow-holes, elongated in the direc-

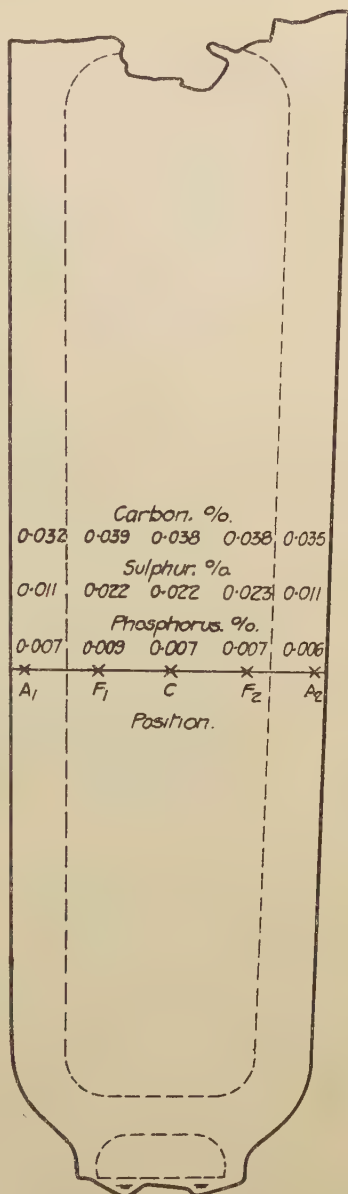


FIG. 3.—Ingot No. 6, Cast H3906. Analyses of samples taken at five positions in the ingot.

tion of solidification, are to be seen throughout the rim. The core structure shows a coarser equi-axed grain with central porosity and small irregular blow-holes at the core-rim junction.

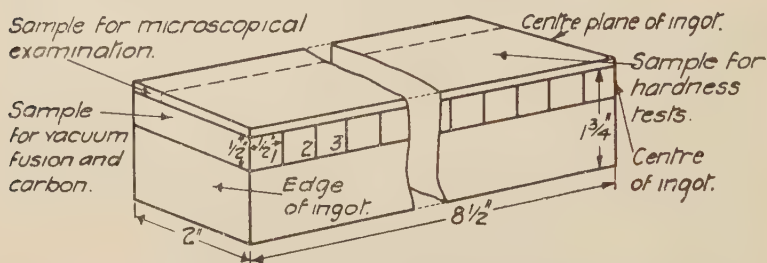


FIG. 4.—Ingot No. 6, Cast H3906. Method of taking samples.

(2) *Microscopical examination* is confined to a general review of the distribution and types of inclusions present. In the rim they were minute and globular, with occasional larger films of oxide; the distribution was of a random character, with occasional evidence of cellular formation. Traversing the rim from the outside, an increase in the size of the inclusions with a decrease in their number towards the rim-core junction was observed. The following types of inclusions were seen :

(a) Minute globular particles of silica glass, confined to the edge of the ingot.

(b) Small globular particles of oxide-silicates—mixed (Fe-Mn)O with silica.

(c) Duplex oxide-sulphides.

(d) Oxide films (probably FeO).

(e) A few small groups of minute inclusions, probably  $\text{Al}_2\text{O}_3$ .

No segregation was evident around the blow-holes in the rim. Towards the rim-core junction the inclusions were larger, consisting of oxide-sulphides in a random distribution, with occasional small groups of minute inclusions (probably  $\text{Al}_2\text{O}_3$ ). Some comparatively slight segregation was seen round the rim-core junction blow-holes, the inclusions being larger, with non-sulphide inclusions present. The larger duplex oxide-sulphide inclusions in the rim persisted throughout the core, with no evidence of a change in character. As in the Denain ingot, Example No. 64 (reported upon fully in the Ninth Report on Steel Ingots<sup>(2)</sup>), etched specimens showed that, in the slice of ingot No. 6, cast H3906, the inclusions were remote from the crystal boundaries. Photographs of typical groups of inclusions in the rim (2 in. from the edge) and in the core (6 in. from the edge) are shown respectively in Figs. 10 and 11.

(3) *Hardness determinations*, using a 2-mm. dia. ball and 40-kg.

load with the Vickers machine, were carried out on the face of the ingot slice at  $\frac{1}{4}$ -in. intervals. The results are presented graphically in Fig. 5, and, as in the examination of previous rimming-steel

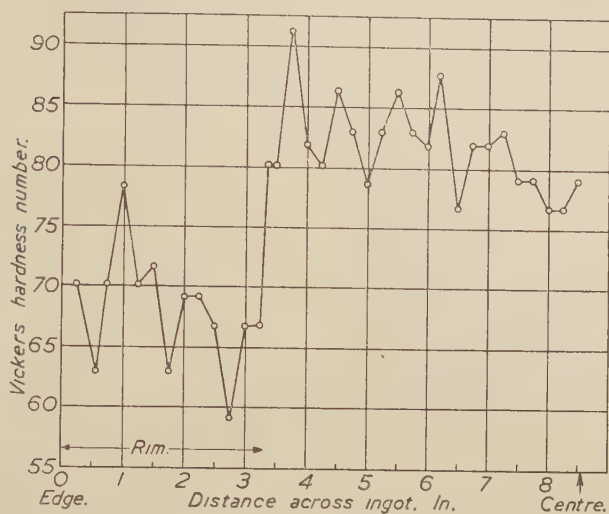


FIG. 5.—Ingot No. 6, Cast H3906. Hardness values of central section across the face (2-mm. ball, 40-kg. load).

TABLE II.—Ingot No. 6, Cast H3906, Carbon, Oxygen, Hydrogen and Nitrogen Analyses on Samples taken at  $\frac{1}{2}$ -in. Intervals from Edge to Centre.

Sample No.	Carbon. %.		Oxygen. %.		Hydrogen. ML. per 100 g.		Nitrogen. %.	
	Original Slice.	Adjacent Slice.	Original Slice.	Adjacent Slice.	Original Slice.	Adjacent Slice.	Original Slice.	Adjacent Slice.
No. 1 (edge)	0.039	...	0.020 <sub>6</sub>	...	0.15	...	0.001 <sub>6</sub>	...
2	0.024	...	0.015	...	0.40	...	0.001 <sub>2</sub>	...
3	0.020	...	0.012 <sub>3</sub>	...	1.00	...	0.000 <sub>3</sub>	...
4	0.018	...	0.010	...	1.02	...	0.000 <sub>4</sub>	...
5 5a	0.015	0.015	0.009 <sub>5</sub>	0.011 <sub>5</sub>	1.25	1.50	0.000 <sub>5</sub>	0.001 <sub>5</sub>
5b	...	0.022	...	0.010 <sub>5</sub>	...	1.80	...	0.002 <sub>5</sub>
6	0.021	...	0.010 <sub>7</sub>	...	1.85	...	0.001 <sub>5</sub>	...
6a	...	0.025	...	0.028	...	2.86	...	0.003 <sub>6</sub>
7	0.028	...	0.041 <sub>6</sub>	...	2.58	...	0.003 <sub>6</sub>	...
7a	...	0.033	...	0.036	...	0.85	...	0.003 <sub>7</sub>
8a	0.034	0.034	0.036	0.036	0.50	0.20	0.003 <sub>8</sub>	0.004 <sub>8</sub>
9	0.037	...	0.036	...	0.75	...	0.003 <sub>9</sub>	...
10	0.033	...	0.037	...	0.83	...	0.002 <sub>9</sub>	...
11	0.036	...	0.040 <sub>4</sub>	...	1.05	...	0.003 <sub>1</sub>	...
12	0.036	...	0.036 <sub>1</sub>	...	1.08	...	0.003 <sub>9</sub>	...
13	0.038	...	0.036 <sub>2</sub>	...	0.55	...	0.003 <sub>2</sub>	...
14	0.040	...	0.035 <sub>2</sub>	...	0.86	...	0.002 <sub>4</sub>	...
15	0.038	...	0.035 <sub>2</sub>	...	1.17	...	0.003 <sub>2</sub>	...
16	0.038	...	0.042	...	0.85	...	0.011 <sub>6</sub>	...
17 (centre)	0.038	...	...	...	0.80	...	0.010 <sub>5</sub>	...



samples, the hardness values correspond broadly to the composition at the respective positions.

(4) The results of *oxygen, hydrogen and nitrogen determinations by vacuum fusion and of carbon determinations* on the section at intervals of approximately  $\frac{1}{2}$  in. are given in Table II. and plotted graphically in Fig. 6. The samples are numbered 1 to 17 from the

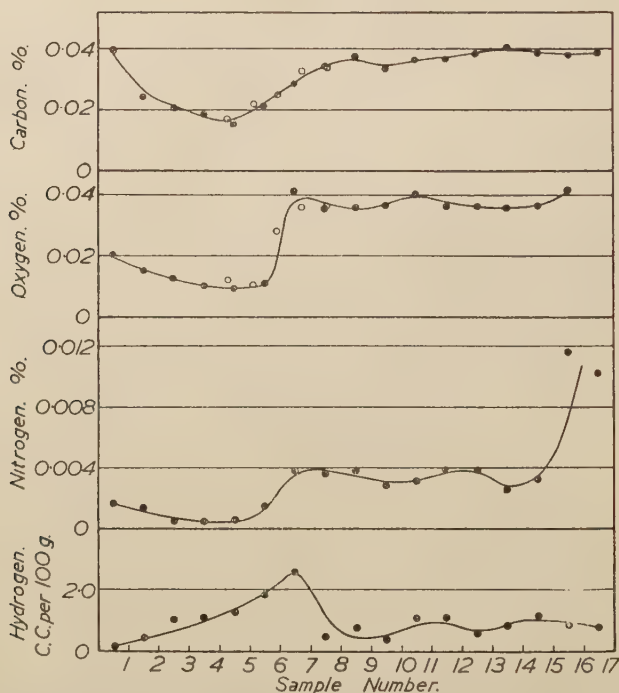
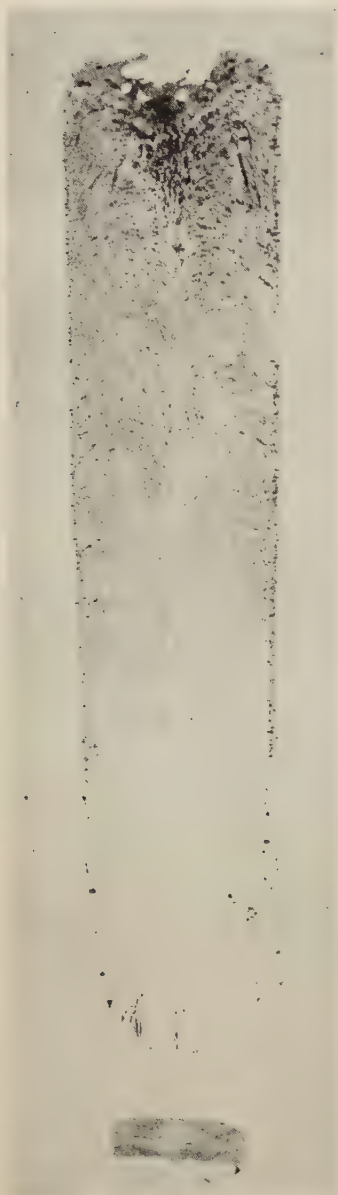


FIG. 6.—Ingot No. 6, Cast H3906. Variation of carbon, oxygen, nitrogen, and hydrogen across a central slice.

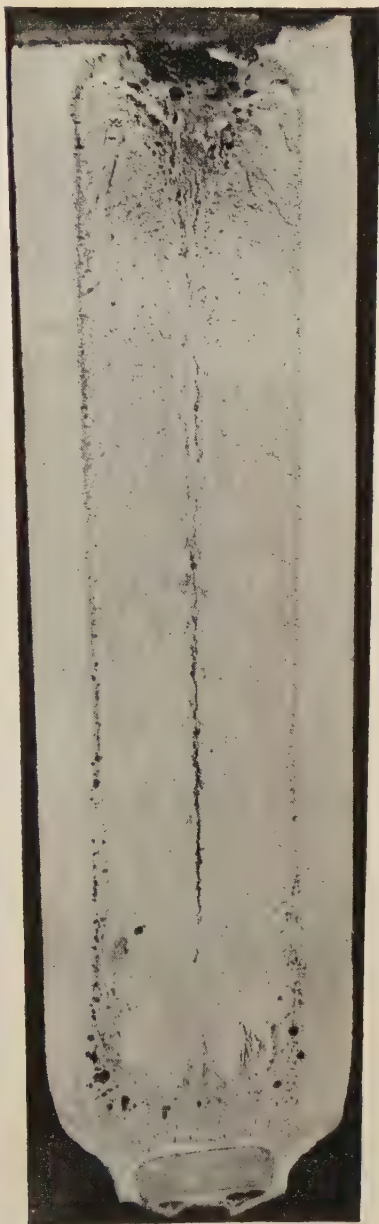
outside to the centre, each number representing a distance of  $\frac{1}{2}$  in. Five additional samples were also analysed for check purposes from adjacent positions in the rim-core junction zone. These five samples are denoted 5a, 5b, 6a, 7a and 8a, and are shown in Fig. 6 as unfilled circles, the original seventeen samples appearing as black circles; the distance covered by the five samples in the ingot section is exactly equal to that covered by the samples 5, 6, 7 and 8. The former thus represent intervals of 0.4 in., against 0.5 in. for the original series of samples.

#### Observations on the Results.

Interest centres chiefly around the carbon-oxygen distribution



(a) Sulphur Print.



(b) Macro-Etching.

FIG. 8.—Ingot No. 6, Cast H3906.

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(a) Sulphur Print.



(b) Macro-Etching.

FIG. 9.—Slice from Middle of Ingot No. 6, Cast H3906.

(a)  $\times 150$ .(b)  $\times 800$ .

FIG. 10.—Ingot No. 6, Cast H3906. Distribution and type of inclusions in the rim.

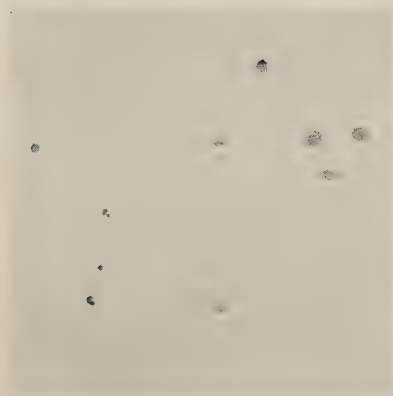
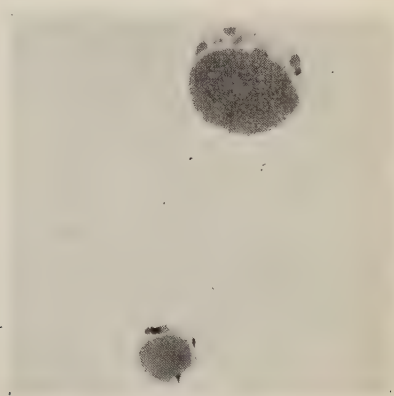
(a)  $\times 150$ .(b)  $\times 800$ .

FIG. 11.—Ingot No. 6, Cast H3906. Distribution and type of inclusions in the core.

(Micrographs reduced to four-fifths linear in reproduction.)

Top Section, T.I.

Middle Section, R.2.

Face M.

Face N.



Sulphur  
Print.

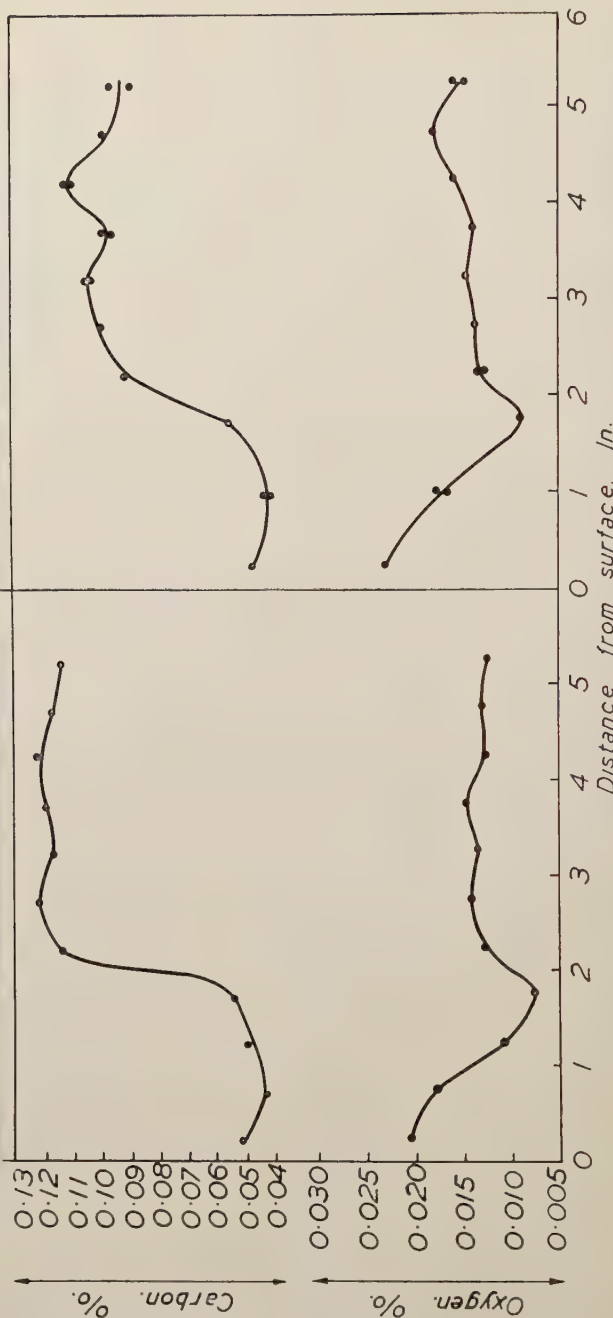


FIG. 12.—Cast 31/8940. Variation of carbon and oxygen at two sections, corresponding to positions two-thirds and one-third of the height from the bottom of the ingot.

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in its bearing on the Hultgren-Phragmén hypothesis, but other features may briefly be noted first.

The first point is that this steel is comparatively free from blow-holes at the junction of the rim and core. The type and distribution of inclusions do not differ materially from those of other examples of rimming steel examined, notwithstanding that this ingot is substantially lower in sulphur and higher in oxygen contents.

The distribution of nitrogen follows the same form of curve as before, being consistently low across the rim, rising to a higher figure at the junction with the core and maintaining this higher figure across the core. Towards the dead centre of this ingot two abnormally high values are recorded. These are in the region of central porosity and may be unreliable, but, on the other hand, it is possible that they do represent a segregation of nitrogen in this particular type of steel.

The hydrogen values are distinctly lower than in cast 34/8940, which is not unexpected in view of the higher oxygen values. Whilst, in the light of present knowledge of the effect of the time element, sample preparation and method of determination, the hydrogen values cannot be regarded as absolute, the trend of the results may be accepted as reliable. The content rises steadily through the rim to a peak and then falls to a lower value throughout the core approximately at the level of the average through the rim. This provides an interesting contrast to the results on cast 34/8940, where the hydrogen in the core was distinctly higher than that in the rim.

Reverting now to the carbon-oxygen distribution, the curves for *H3906* have reversed their characteristics as compared with cast 34/8940. Taking equivalent positions in the ingots, in the latter, with a pit-sample carbon content of 0.10% (*i.e.*, above the balanced composition), the carbon is consistently low in the rim, rising steeply to a maximum very considerably higher, which is maintained through the core—*see* Fig. 12. The average values are 0.047% of carbon in the rim and 0.106% in the core.

In *H3906*, however (*see* Fig. 6), with a pit-sample carbon content of 0.047%, the carbon is steadily reduced through the rim, and rises steadily to a higher value, which is maintained through the core but barely reaches the value of the outer rim and is actually below the pit-sample value. The average values of rim and core are respectively 0.025% and 0.037% of carbon.

The oxygen values are still more striking, again taking equivalent ingot positions. In cast 34/8940 (*see* Fig. 12) the highest content is in the outer rim (0.022%); this falls gradually through the rim to 0.008%, and rises at the junction to a medium value of about 0.014%, which is then maintained throughout the core. In *H3906*, however (*see* Fig. 6), while the oxygen in the outer rim is practically the same at 0.020%, and the value falls gradually through the rim to about 0.010%, it rises steeply at the junction to about 0.040% and maintains *this* value throughout the core. Thus, in contrast to 34/8940, the average oxygen in the core is about 3 times that of the rim.

In Fig. 1 is reproduced diagrammatically the Hultgren-Phragmén hypothesis, and in Fig. 2 it is shown that the carbon-oxygen relationship from outside to centre for cast 34/8940, with a pit-sample carbon content of 0.10%, forms a curve of the type outlined by line *PBD*.

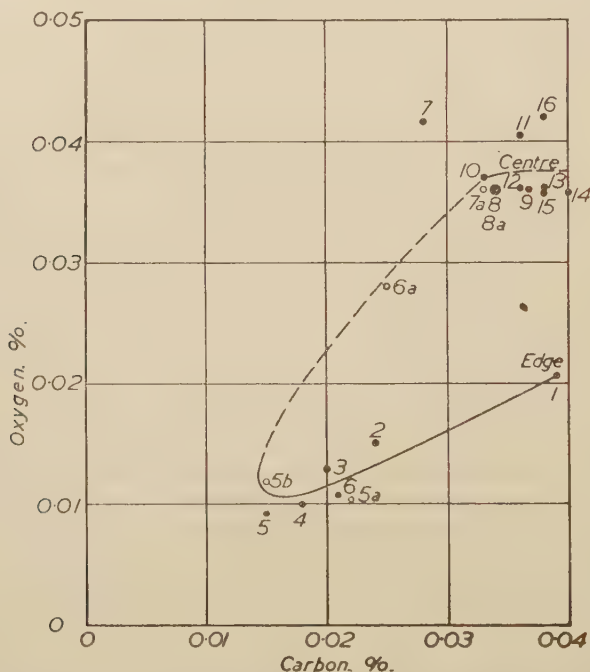


FIG. 7.—Ingot No. 6, Cast H3906. Ratio of total oxygen to carbon values (see Table III.). The numbers represent the positions from outside to centre of the ingot.

In Fig. 7, plotted in a similar manner, the curve for cast H3906, with a pit-sample carbon content of 0.047%, follows the reverse order, as indicated by line *QEF* in Fig. 1. The samples are numbered 1 to 16 from outside to centre; the black circles represent the original samples examined, and five additional checks (shown as hollow circles) were made in the vicinity of the rim-core junction to mark with more certainty the path of this curve. Thus, although the differences in composition are comparatively small, sample 6a, for example, appears to indicate quite definitely the direction of the "return" portion of the curve.

It is submitted that these data provide excellent verification of the hypothesis postulated by Hultgren and Phragmén. Furthermore, the actual values for carbon and oxygen representing the

balanced composition, namely, 0.06% of carbon and 0.04% of oxygen, appear to be substantially correct.

The sampling of liquid steel of this type for accurate oxygen determinations is now on a reasonably satisfactory basis, and work is in hand to provide more extensive data on the actual carbon and oxygen contents of ladle metal representative of rimming steel in normal production.

#### *Acknowledgment.*

The tedious nature of this work in determining very small contents of carbon and small variations of other elements will readily be recognised, and the author takes pleasure in paying tribute to the staff of the Central Research Department, Stocksbridge, for the work done in this direction and in the metallurgical survey. He also expresses his thanks to The United Steel Companies, Ltd., for the facilities provided and for permission to publish the results.

#### APPENDIX.

The results of the vacuum fusion tests reported in this paper represent *total* oxygen. The fractional vacuum fusion method has been further developed in the author's laboratories since the publication of the previous two papers<sup>(1, 2)</sup> on rimming steel. The fractional method has been applied to a sample from the rim and another from the core of ingot No. 6, cast H3906, to throw further light on the constitution of the oxides present in rimming steel. These two samples were taken from positions 2 in. from the edge of the ingot (in the rim) and 6 in. from the edge of the ingot (in the core); the results obtained are recorded in Table III.

TABLE III.—*Ingot 6, Cast H3906, Fractional Vacuum Fusion Determinations.*

Fraction.	Oxygen. %.	Oxide. %.	Hydrogen. Ml. per 100 g.	Hydrogen. %.	Nitrogen. %.
<i>Sample No. 4 (in the Rim).</i>					
FeO } . .	0.008 <sub>7</sub>	0.038 <sub>5</sub> *	1.16	0.0001 <sub>0</sub>	...
MnO } . .			0.10	0.0000 <sub>1</sub>	0.0001
SiO <sub>2</sub> . .	...	...	...	...	...
Al <sub>2</sub> O <sub>3</sub> . .	...	...	...	...	0.000 <sub>6</sub>
Total . .	0.008 <sub>7</sub>	0.038 <sub>5</sub>	1.26	0.0001 <sub>1</sub>	0.000 <sub>7</sub>
<i>Sample No. 12 (in the Core).</i>					
FeO } . .	0.033 <sub>4</sub>	0.148 <sub>5</sub> *	1.20	0.0001 <sub>1</sub>	0.0001
MnO } . .			0.10	0.0000 <sub>1</sub>	0.0002
SiO <sub>2</sub> . .	0.0004	0.0007	...	...	...
Al <sub>2</sub> O <sub>3</sub> . .	0.0007	0.0015	...	...	0.0028
Total . .	0.034 <sub>5</sub>	0.150 <sub>7</sub>	1.30	0.0001 <sub>2</sub>	0.0031

\* Obtained by using an average factor for conversion of oxygen to FeO + MnO.

In comment on these results, it will be noted that :

(a) The sum of the fractions approximates closely to that of the total-oxygen figure obtained on samples taken at immediately adjacent positions.

(b) The oxides of iron and manganese preponderate strongly.

(c) No measurable amounts of the silica and alumina fractions are found in the sample from the rim zone. Very small amounts of these two fractions are present in the sample from the core zone.

(d) Previous observations are confirmed respecting hydrogen and nitrogen, in that the bulk of the former is evolved in the early fraction, whilst the bulk of the latter is evolved in the last fraction. The higher nitrogen content in the core, as compared with the rim, is also confirmed.

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- (4) EDWARDS : Ninth Report on the Heterogeneity of Steel Ingots, p. 1, *Iron and Steel Institute*, 1939, *Special Report No. 27*.
- (5) MYERS : Swansea Technical College Metallurgical Society, Jan., 1939.
- (6) Sixth Report on the Heterogeneity of Steel Ingots, p. 23, *Iron and Steel Institute*, 1935, *Special Report No. 9*.

[This paper was discussed jointly with the preceding one by D. Binnie on "An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process" and two by J. Mitchell on "Rimming Steel" and the following one by T. Swinden and W. W. Stevenson on "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C."]

# A NOTE ON DIFFUSION IN RIMMING STEEL ON SOAKING AT ABOUT 1300° C.\*

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(Figs. 3 to 10 = Plates XXXIV. to XXXVII.)

*Paper No. 16/1942 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

This note deals with the effect of reheating for 46 hr. at about 1300° C. a 7½-in. square bloom section of 0.09% carbon rimming steel.

There is a very slight diffusion of carbon from the core to the rim zone. There is no apparent migration of sulphur from the core to the rim; in fact, the rim-core demarcation is even more sharply defined on the sulphur print after treatment than before.

Some interesting observations are made on the changes in constitution and distribution of the inclusions, particularly within the core zone.

SECTIONS of rimming steel, varying in size from the ingot weighing several tons down to rod and strip of small cross-section, all exhibit a familiar sharp dividing line at the junction of the rim and core zones. It has been shown that in rimming steel of which the pit sample carbon content is of the order of 0.10% the average carbon content of the rim zone is about 0.05% and that of the core zone about 0.11%. In order to ascertain the extent to which diffusion of carbon, if any, would take place at the junction of these zones of dissimilar carbon contents, the authors subjected a bloom section of fully rimmed steel to prolonged heating at elevated temperature.

A bloom section, 1½ in. thick × 7½ in. square, was selected from cast 31/660 of the following pit sample analysis :

Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.
0.09%	0.34%	Trace	0.035%	0.017%

The section was heated between refractory bricks in a mill furnace for 46 hr. at 1300° ± 20° C. A comparable section, cut from an immediately adjacent position in the bloom, was retained for examination in the untreated condition.

After the soaking treatment, the bloom section was planed on

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both cut faces and the face adjacent to the comparative section was sulphur-printed along with the latter. Photographs of the

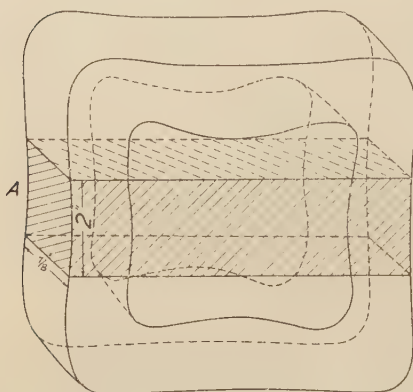


FIG. 1.—Method of taking Sections from Untreated and Treated Rimming-Steel Blooms.

sulphur prints are reproduced in Fig. 3. The core-rim junctions on the left-hand sides of the sections are almost a straight line and a 2-in. wide piece,  $1\frac{1}{4}$  in. thick, was therefore cut from the centre of this side, after cutting a thin slice for microscopical examination. The piece was then planed to yield ultimately a section  $7\frac{1}{4}$  in.  $\times$  2 in.  $\times$   $\frac{7}{8}$  in., as shown in Fig. 1.

Starting at the left-hand edge, A, of the section, millings were taken at  $\frac{1}{32}$ -in. intervals until 80 such samples were obtained over a distance of  $2\frac{1}{2}$  in. Samples numbers 20 to 55, covering more than  $\frac{1}{2}$  in. on either side of the core-rim junction, were analysed for carbon, with results as given in Table I.; they are also reproduced graphically

TABLE I.—Carbon Contents of Successive  $\frac{1}{32}$ -in. Layers Milled from Sections of Untreated and Treated Rimming-Steel Bloom.

Sample No.	Carbon. %.		Sample No.	Carbon. %.	
	Untreated Billet.	Treated Billet.		Untreated Billet.	Treated Billet.
20	0.045	0.04	39	0.065	0.075
21	0.04	0.045	40	0.08	0.075
22	0.045	0.04	41	0.095	0.08
23	0.045	0.05	42	0.09	0.085
24	0.045	0.05	43	0.105	0.09
25	0.045	0.045	44	0.105	0.09
26	0.05	0.045	45	0.105	0.10
27	0.05	0.045	46	0.12	0.10
28	0.05	0.045	47	0.12	0.11
29	0.045	0.045	48	0.12	0.115
30	0.05	0.045	49	0.115	0.10
31	0.045	0.05	50	0.12	0.12
32	0.05	0.05	51	0.125	0.115
33	0.05	0.055	52	0.135	0.105
34	0.05	0.055	53	0.115	0.11
35	0.055	0.06	54	0.11	0.105
36	0.055	0.06	55	0.115	0.10
37	0.06	0.07	56	0.125	0.115
38	0.065	0.07			

in Fig. 2. In view of the alteration in appearance of the sulphur prints of the untreated and treated sections, a few selected samples

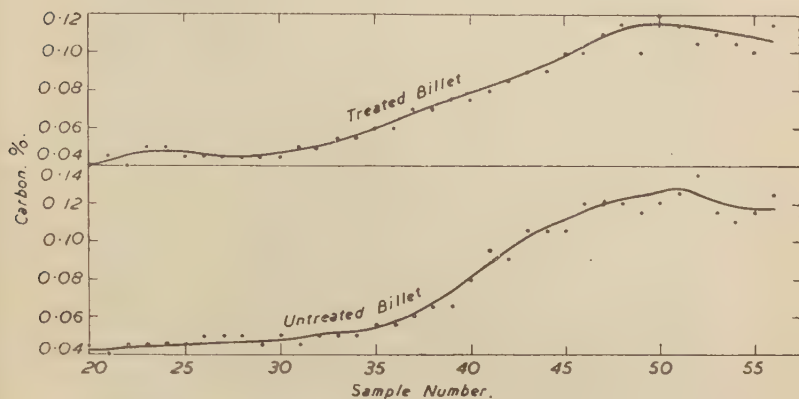


FIG. 2.—Carbon Contents of Successive Samples Milled at  $\frac{1}{32}$ -in. Intervals from Untreated and Treated Rimming-Steel Blooms.

were analysed for sulphur; the results obtained are given in Table II.

TABLE II.—Sulphur Contents of Selected Samples from Untreated and Treated Sections of  $7\frac{1}{4}$ -in. square Rimming-Steel Bloom.

Sample Nos.	Distance from Edge of Section. In.	Position.	Sulphur. %.	
			Untreated Section.	Treated Section.
7, 8	$\frac{1}{4}$	Just inside rim.	0.018	0.020
30, 31, 32	1	In rim, near rim-core junction.	0.023	0.023
50, 51, 52	$1\frac{5}{8}$	Just inside core.	0.073	0.101
79, 80	$2\frac{1}{2}$	Inside core.	0.069	0.072

The *sulphur print* of the *untreated* section of the  $7\frac{1}{4}$ -in. square billet (Fig. 3(a)) shows a deep and slightly irregular rim of depth varying from  $1\frac{3}{8}$  in. to  $1\frac{1}{2}$  in., with the sulphur content increasing slightly towards the rim-core junction. The *treated* section (Fig. 3(b)) shows a similar depth and variation in thickness of the rim, with more uniform distribution of sulphur in the rim. Within the core, coalescence and globularisation of the small sulphur segregates has occurred. There is no evidence of sulphur diffusion having taken place outwards from the core to the rim.

*Microscopical Examination of Inclusions.*

It was not within the immediate scope of this experiment to go beyond an observation of the effect of a prolonged soak at about 1300° C. on the general configuration of the rim and core boundary and to note any movement, particularly of carbon and sulphur, across this boundary.

Time has not been available, under the present stress of other work, to study in detail the effect on the inclusions in the exhaustive way that Whiteley <sup>(1)</sup> did in his excellent study in this field. Nevertheless, the following observations have been made, and it may be possible to elaborate these somewhat at a later date.

In the *outer zone* of the *rim*, which extended to a maximum depth of  $\frac{5}{8}$  in. from the edge of the bloom, the inclusions were mainly small streaks and globules having a random distribution. They consisted of small particles of oxides, occasional larger oxide-silicates, and small particles of sulphide. *Reheating* had not affected the distribution of the inclusions, but the streaks had been converted to small stringers of globular oxide, with fewer oxide-sulphides.

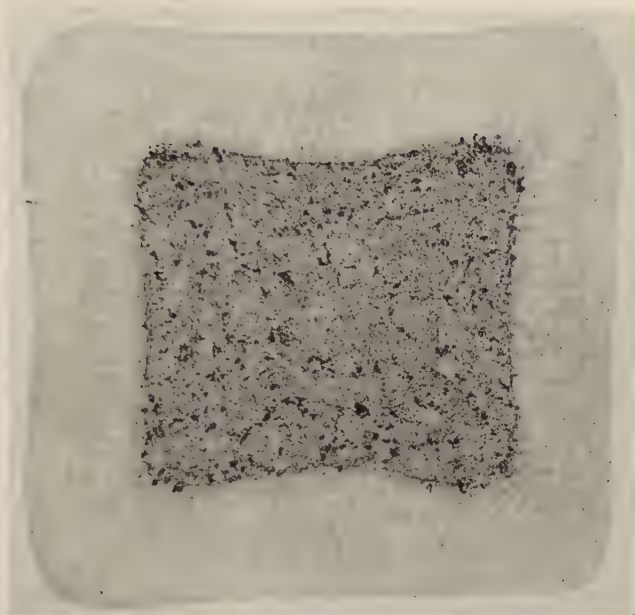
In the *inner zone* of the *rim*, the inclusions were slightly more numerous, increasing as the core was approached; they were generally slightly larger in size in this zone, with a similar random distribution. The streaks consisted mainly of duplex oxide and sulphide of the (Mn,Fe)S type. Smaller and fewer streaks of duplex sulphide type, consisting of MnS and (Mn,Fe)S, were present. Occasional larger silicate streaks and numerous small globular oxides were evident. *Reheating* had not altered the distribution, but had changed the streaks into small stringers of the globular duplex oxide-(Mn,Fe)S types.

In the *core* the general distribution of inclusions was less uniform than in the rim, having a tendency to segregate formation. Generally the inclusions were small, but they were larger than in the rim. The streaks consisted of duplex MnS-(Mn,Fe)S and duplex oxide-(Mn,Fe)S types (see Fig. 4), with small globular monophase sulphides. *Reheating* had not varied the general distribution, but most of the streaks, especially those of the duplex oxide-sulphide type, had broken down into stringers of globular duplex particles of oxide-(Mn,Fe)S, but apparently, from their appearance, containing less FeS than the untreated sample (see Fig. 5).

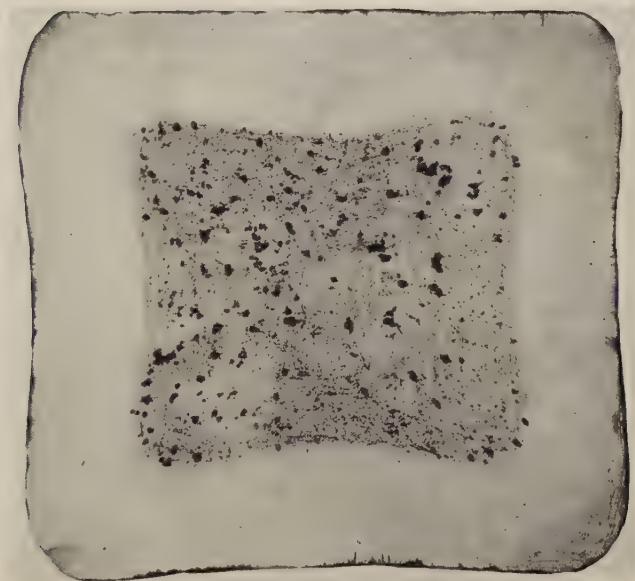
There was a definite tendency in the oxide-sulphide inclusions for the oxide to migrate to the edges as a result of the reheating treatment.

The oxide-free sulphides generally showed less tendency to globularise, and also contained less FeS than similar types of inclusions in the untreated sample (see Fig. 6).

As noted above, and as seen in the sulphur print, Fig. 3(a), the *core* of the *untreated* bloom contained small areas of more concentrated sulphide inclusions. These consisted almost entirely of a partial



(a) Section as Rolled, *i.e.*, untreated.



(b) Section after Soaking for 46 hr. at about 1300° C.

FIG. 3.—Cast 31/660. Sulphur prints of bloom sections.

[Swinden and Stevenson.  
[To face p. 360 p.]

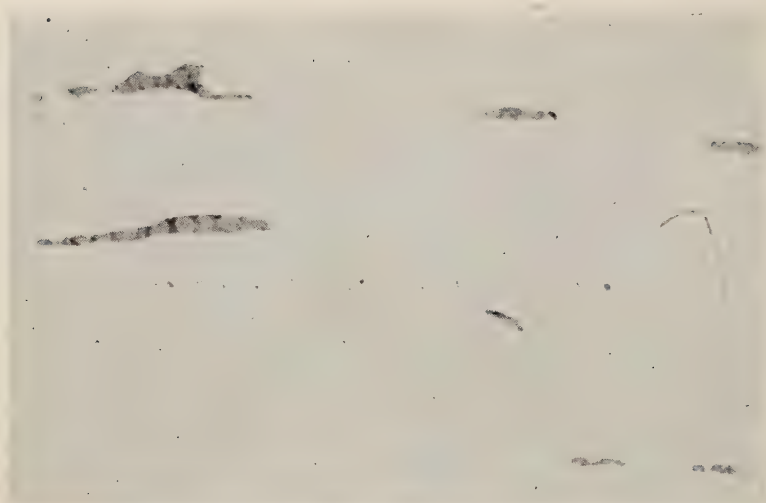


FIG. 4.—Core of Untreated Section, showing duplex  $\text{MnS-(Mn,Fe)S}$  and duplex oxide- $\text{(Mn,Fe)S}$  elongated inclusions, with small globular monophase sulphides.  $\times 300$ .

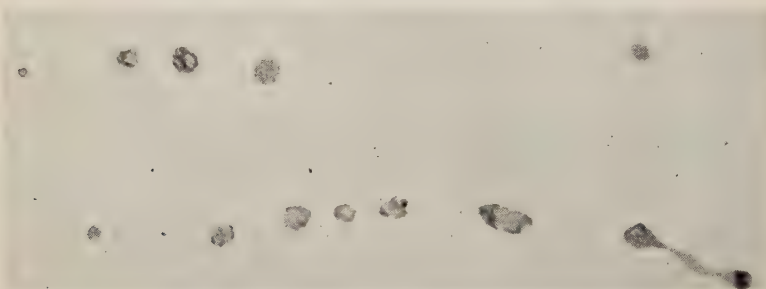


FIG. 5.—Core of Treated Section, showing duplex oxide- $\text{(Mn,Fe)S}$  inclusions in stringers of globules.  $\times 300$ .

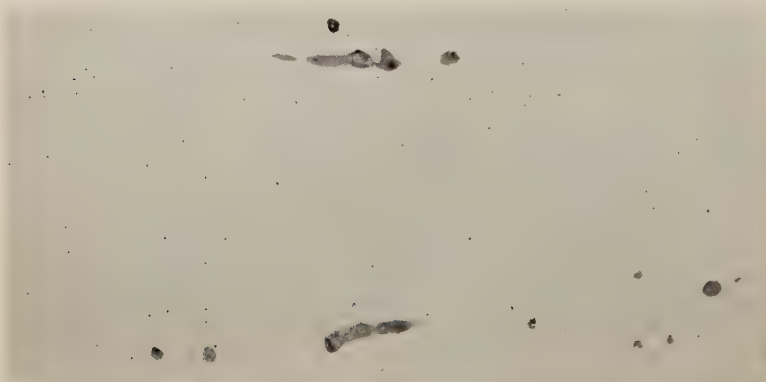


FIG. 6.—Core of Treated Section, illustrating the lesser tendency of the comparatively oxide-free sulphides to globularise.  $\times 300$ .





FIG. 7.—Core of Untreated Section, illustrating a concentration of inclusions consisting of monophase sulphides with a high proportion of FeS.  $\times 300$ .

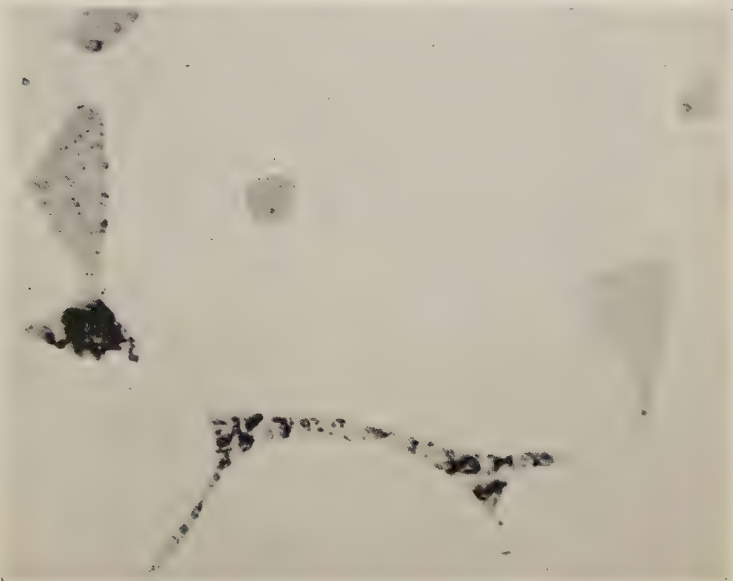


FIG. 8.—Core of Treated Section, illustrating a similar field to Fig. 7 after treatment, showing monophase sulphides with varying concentrations of FeS, but with the latter predominating. The dark areas are due to the pitting of the inclusions rich in FeS. Note the distribution towards the grain boundaries.  $\times 300$ .

[Swinden and Stevenson.]

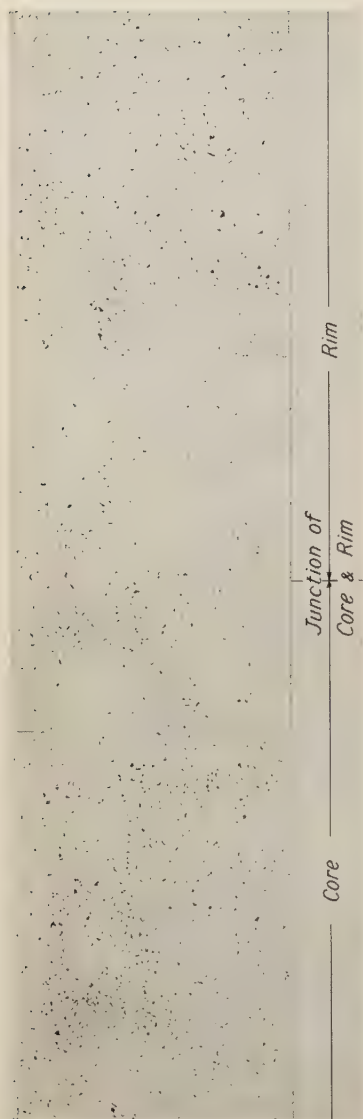


FIG. 9.—Untreated Section.

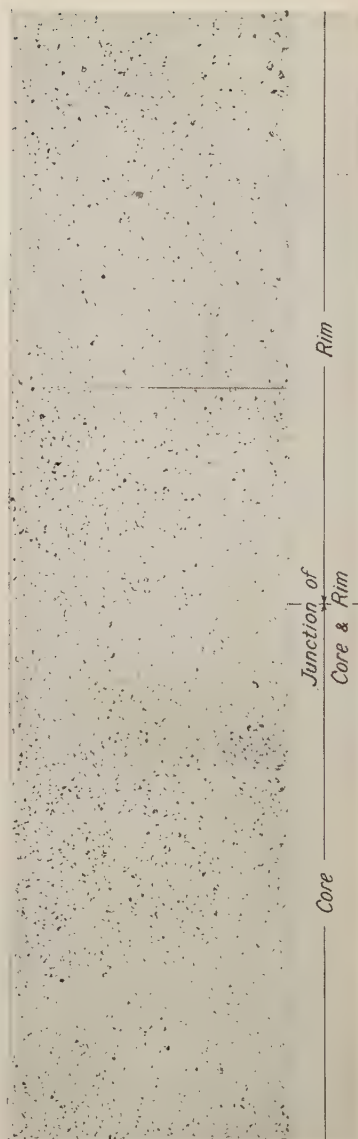


FIG. 10.—Treated Section.

FIGS. 9 and 10.—A Slight Migration of Carbon across the Rim-Core Junction.  $\times 40$  (reduced to half-size linear in reproduction).

[Swinden and Stevenson.  
[To face p. 361 P.

network form of distribution of small globular particles of monophase sulphide containing a high percentage of FeS. A small amount of MnS was also present in these areas (*see* Fig. 7). After *reheating*, the segregates of mixed monophase sulphide had coalesced (note also that the effect is revealed in the sulphur print of the treated section in Fig. 3(b)) and formed (a) large masses of FeS and (b) (Mn,Fe)S inclusions, consisting mainly of FeS (*see* Fig. 8). The masses had dispersed to the boundaries of the large grains present at the reheating temperature. Small globular particles of (Mn,Fe)S, of low FeS content, were also present and had slightly coalesced.

Silicate streaks had remained unchanged by the reheating in both the rim and the core.

Four main points of interest arise from a consideration of the behaviour of the inclusions in rimming steel on reheating, in comparison with similar experiments carried out by Whiteley <sup>(1)</sup> on sections of high-sulphur free-cutting steels.

(1) Although the present experiment was carried out on a bloom section  $7\frac{1}{4}$  in. square, rolled from a  $22\frac{1}{2}$ -in. square ingot, the segregated areas in the core (*see* Fig. 7) show a formation of inclusions not unlike that of Whiteley's "primary formation," obtained by him on reheating sections to 1450° C. This type of formation, however, is more usually associated with ingot material, and a similar grouping of MnS inclusions was described by Portevin and Castro <sup>(2)</sup> as "eutectiform." In the present instance the inclusions had a high content of FeS.

(2) The streaks of oxide-sulphide in the core of the untreated section have become, as a result of the heating treatment, strings of elongated globules of similar width to the original streaks (*see* Figs. 4 and 5). Instead of coalescing, as did sulphide inclusions in segregates in the core, they have apparently broken up and become rounded masses, probably by surface-tension effects. Whiteley <sup>(1)</sup> states that these inclusions (in his examination) belong to the system MnS-FeS-fayalite-rhodenite, with occasional addition of FeO.

(3) The behaviour of the sulphides in the non-segregated areas of the core is normal for a steel containing an excess of manganese over that required to combine with the sulphur present. The effect of the reheating treatment has been that the manganese content of the sulphides has increased. Very little coalescence has occurred, and elongated inclusions have become strings of globules.

(4) In the segregated areas, the treatment has not had the effect of increasing the manganese content of the sulphide inclusions. Already containing high FeS (in the untreated bloom), these sulphides have coalesced, with the separation of FeS, which has dispersed to the grain boundaries. These inclusions would be liquid at the reheating temperature—hence their coalescence and migration. It is quite possible that the increased FeS content of these inclusions is due

to the reaction  $\text{FeS} + \text{Mn} \rightleftharpoons \text{MnS} + \text{Fe}$  proceeding from right to left under the conditions prevailing in the segregated areas of the core. Another likely factor controlling their behaviour is the very slow diffusion of manganese, also pointed out by Whiteley.<sup>(1, 3)</sup>

*Microscopical Examination of Carbide Distribution.*

The appearance of the zones on either side of the rim-core junction is illustrated in Fig. 9 (untreated section) and Fig. 10 (treated section). Whilst in the untreated section there is a comparatively sudden increase in carbon content on passing from the rim to the core, in the treated section there is a much more gradual carbon increase over a distance of more than  $\frac{1}{2}$  in. This confirms the carbon analyses given in Table I. and Fig. 2, showing that the reheating treatment has brought about slight diffusion of carbon from the core to the rim of the bloom.

The authors thank Mr. R. E. Lismer for his painstaking work in the micro-examination reported herein.

REFERENCES.

- (1) GREGORY and WHITELEY : *Journal of The Iron and Steel Institute*, 1941, No. II., p. 15 P.
- (2) PORTEVIN and CASTRO : *Journal of The Iron and Steel Institute*, 1935, No. II., p. 237, Fig. 21.
- (3) WHITELEY : Seventh Report on the Heterogeneity of Steel Ingots, Section 3A, *The Iron and Steel Institute*, 1937, *Special Report No. 16*.

[This paper was discussed jointly with the preceding one by D. Binnie on "An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process," two by J. Mitchell on "Rimming Steel" and one by T. Swinden on "Rimming Steel."]

## JOINT DISCUSSION.

(Fig. A = Plate XXXVIIA.)

The papers by D. Binnie on "An Ingot of Rimmed Steel made by the Basic Open-Hearth Process," by J. Mitchell on "Rimming Steel.—Comparative Study of Three Ingots Received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France," by J. Mitchell on "Rimming Steel.—Report on Four Ingots of Basic Bessemer Steel," by T. Swinden on "Rimming Steel.—Additional Studies of the Composition Variation from Outside to Centre," and by T. Swinden and W. W. Stevenson on "A Note on Diffusion in Rimming Steel on Soaking at about 1300° C.," were discussed jointly.

Dr. W. H. HATFIELD, F.R.S. (Vice-President; Chairman of the Committee on Heterogeneity of Steel Ingots; The Brown-Firth Research Laboratories, Sheffield): I do not wish to take up much of the time of the Meeting, because we are very anxious that this work should be fully discussed by those who have not had the great privilege of joining in the monthly discussions which we have had in the Committee. I should like, however, to submit that we have here this afternoon the results of an ideal form of investigation. You will remember that in the old days we used to buy millions of tons of this and similar kinds of steel from the Continent. That steel was bought under very satisfactory conditions—looked at from the view of the purchaser—and it proved to be excellent rimming steel. It had the virtue which Mr. Mitchell extols in his paper, a good rim, essentially free from blow-holes. It was so interesting that the Committee as a body thought that it would be serviceable to the iron and steel industry of Great Britain if we could secure from the Continent samples of this rimming steel in ingot form and study completely the characteristics of the ingots.

Our Continental friends were very kind and broadminded. They let us have ingots of rimming steel, and the initial and subsequent investigations are to be found recorded in the *Journal* of our Institute.

It had always been a mystery that in steel of this character there was an excellent thick rim of pure steel, but having investigated these ingots we as a Committee were not satisfied to let the matter rest there, and all the major works of Britain have joined up to see whether by collective effort the many aspects of the matter could be tackled. The Institute has had a number of papers on rimming steel already, and this afternoon we have a magnificent group of new ones, all of them prepared under the ægis of the Committee.

Dr. Binnie's paper is masterly in the knowledge that it displays of physical chemistry at high temperatures and in its consideration of the Hultgren and Phragmén theory. It would be of value if to



the data given in the paper he could add the oxygen contents of the samples. Dr. Swinden or I would be very pleased to put those oxygen determinations through, because then the data would be made a little more complete.

Mr. Mitchell's contributions are invaluable, putting before us, as they do, the practical consideration of these matters which he was kind enough to undertake.

Finally, there is the excellent work of Dr. Swinden showing the changing composition from the outside of the ingot inwards in the region of the rim. The investigation in which he exposed rimming steel to a temperature of 1300° C. for over 40 hr. to see the extent of the diffusion which took place is a very noteworthy piece of work. The results, so carefully scheduled and presented, constitute a body of real evidence applicable not only in rimming steel but in a far wider field, enabling us to understand what takes place in the solid state at high temperatures.

As you know, Mr. President, in any effort which is made to provide for the execution of collective research in a great industry like ours, it has always to be borne in mind that the secret of success lies in making observations in an atmosphere in which men are willing to exchange ideas. It is not a business matter at all, it is hardly an economic matter, it is a scientific matter, it is a case of men engaged in like problems joining together and freely and frankly saying "I think this; what do you think?" and then as a result of discussion, seeking to extend their knowledge. If the data are not available, then one or other of them offers to do the experiment. Here we have, then, what I regard as a very typical example of how a great industry should seek to extend the background of knowledge so essential to it.

When I come to the essential problem arising out of all these papers, namely, the ultimate true explanation of the formation of this rimming, I feel that all honour is due to Hultgren and Phragmén. They have put forward a very interesting theory, worthy of them and of their country, and I think it can be said that the evidence to date does not contradict that theory. On the other hand, there are still points which are not completely solved, and I think there is a feeling yet that it is not so easy to explain the great drop between the average composition and that of the outer layers constituting the rim. By that I mean that as the liquid steel freezes on the face of the mould the first clusters of molecules are freezing almost instantaneously, but there is a drop—I am speaking from memory—of 30 or 40% in the carbon content.

Dr. T. SWINDEN : It depends on the original carbon figure.

Dr. HATFIELD : I know, but this must apply to all carbon values and it must apply to those curious anomalous cases where we get rimming in steels of very substantial carbon content. I

have discussed these matters in Committee so long that I will not take up more time. All I want to do at this stage is to congratulate the authors on the demonstration they have given of what can be done in implementing so important a subject.

Mr. A. ROBINSON (Hon. Member of Council; Appleby-Frodingham Steel Co., Ltd., Scunthorpe) : The mechanics of rimming steel now seem to be fairly well understood, and the confirmation of the Hultgren and Phragmén hypothesis gives the steelmaker further knowledge of his materials and of what to expect. I think the report by Mr. Mitchell on four different-sized ingots is a most interesting piece of work and shows how the thickness of the rim is limited. We do not seem to be able to get a very much thicker rim with a bigger ingot. The reason for that is probably the rate of cooling through the ingot, and perhaps the velocity of the diffusion of the different impurities in the steel towards the centre.

A rimming steel is apparently made up of a pure rim and of what I would not call a dead steel but a semi-killed steel. The inside of these ingots seems to be a typical semi-killed steel with, in some cases, the typical V or Y form of segregates in the top. The formation of the Y-segregate is not a good thing, because an ingot of that type is always more or less unsound and there has to be a very big discard from it. Judging from the illustrations in the paper (pp. 295 *P et seq.*) ingot No. 64 from Denain would seem to be the best ingot, in spite of the fact that it had a very slow rimming action, and it is interesting to know that one can get a good rimming ingot with very little rimming action that can be seen.

Dr. W. H. HATFIELD, F.R.S. : Very little evolution of gas apparently.

Mr. ROBINSON : I think the casting temperature of rimming steel is also a very important point. Rimming steel may be too hot when teemed. I have seen on the Continent scrap being put into the ingots to start the rimming action, and it is definitely a fact that it will do so and will start a very strong action. As far as I could see, the steel was none the worse for it. It may have been that in putting lengths of scrap in they put in also some oxide as scale. The scrap was not particularly clean, but it was not dirty.

The question for the steelmaker is which is the best type of rimming-steel ingot, the type which has a higher-carbon core or a lower-carbon core? It would be interesting to find out which type of steel is the best in processing. There is no doubt that it is much easier to make rimming steel in the Bessemer converter than in the open-hearth furnace, and much easier to make it in the open-hearth furnace with a shallow bath than with a deep bath. Probably the answer to Mr. Mitchell's question is that in the

Bessemer converter there is very intimate contact between the oxygen and the steel and in the open-hearth furnace there is not the same intimate contact. To make rimming steel in an open-hearth furnace one has to have a very good boil. There may be something in the fact that in the open-hearth furnace the manganese in the bath is usually higher than in the Bessemer converter. The carbon is also more difficult to get down to the low percentage which one can get in the converter. Both manganese and carbon are strong deoxidants and may prevent steel from having the same amount of oxygen in it at the end to help the rimming action.

Professor J. H. ANDREW (Member of Council; Sheffield University): I shall confine myself to the paper by Dr. Swinden and Mr. Stevenson on the diffusion of carbon. I should like to point out to them that if they will refer to Fig. 2 they will find that on superimposing the two curves which represent the carbon content from the rim to the centre of the ingot, the two curves lie on one another up to about sample No. 40, which means that practically no carbon diffused into the rim at all. Beyond that point the superimposition reveals certain differences. I suggest that some of the dark patches shown in Fig. 10 are really significant of the cavities formed by the reaction product of carbon and oxide. That is rather borne out by Fig. 6, showing the slag particle where certain black masses give one the impression that these have been reduced and have fallen out on polishing. Does Dr. Swinden not think that the reactions of the carbon and oxide inclusions are more responsible for loss of the carbon in the centre than diffusion of carbon to the rim? Would he expect carbon in that small amount to have a very high reactivity so far as diffusion is concerned?

Dr. H. A. DICKIE (Messrs. Stewarts and Lloyds, Ltd., Corby): I agree with Dr. Hatfield that we now have a singularly complete and accurate set of data on which to consider the solidification of rimming steel; they are now more extensive than at any previous time, and I think, particularly, that if Hultgren and Phragmén had had such exact data when they wrote their paper they would have come to a more accurate final conclusion in regard to the balanced composition. The paper by Hultgren and Phragmén is an extremely good one, as everybody recognises, but how they managed to come to the peculiar values of 0.06% of carbon and 0.04% of oxygen for the balanced composition is beyond me, and no one has yet suggested why they should choose those values.

The papers at present before the Meeting show in every case—leaving out Dr. Swinden's contribution for the moment—that steels of 0.06% carbon are well above the balanced composition. Mr. Mitchell's four Corby ingots have a pit-sample carbon content of 0.055%, and the carbon content inside the junction, which is the

correct place to make the assessment, is well above the pit-sample analysis. All three of the Denain ingots reported on by Mr. Mitchell are above the balanced composition in carbon; there is one which contains about 0.05% of carbon or slightly lower, but that is above the balanced composition.

Let us consider for a moment what happens in rimming steel. Gas comes off which is mainly carbon monoxide and contains 16 parts by weight of oxygen to 12 of carbon. Some carbon dioxide, possibly about 4%, also comes off, which raises the proportion of the emerging oxygen. Any small amount of methane coming off would tend to wipe out the oxygen content in the carbon dioxide. Assuming for the moment that the first metal to separate in the rim is pure iron, then the only composition that one can have for the balanced composition is one which has the same proportion of oxygen and carbon as the gases coming off.

But there is another necessity to be considered if it is required to have, as in a balanced composition, a liquid which will remain unaltered during the rimming process. It is necessary to have the carbon-oxygen product at atmospheric pressure equal to 0.0025. With these requisites a balanced composition is reached very similar to that given by Dr. Binnie in Table II. of his paper for "nil manganese," *i.e.*, 0.045% carbon and 0.056% oxygen. Actually I think the carbon should be a little lower, something between the figure given and 0.040%.

On the question of whether pure iron separated out during the rimming process, we might get a line on this by taking figures not given in any of the papers but calculated from the data which the papers afford, namely, the carbon-oxygen ratio just outside and just inside the junction—that is to say, more or less the least concentrated and the most concentrated portions. We find that in all the ingots at present under consideration the carbon-oxygen ratio outside and inside the junction is very similar, just as close in any individual ingot as one could reasonably expect from the experimental evidence of this character where the values are changing from point to point. The interesting thing is that, comparing different ingots, these ratios vary enormously: for example, from unity to perhaps 6.

These facts indicate that any carbon and oxygen present in the rim arise from entrapped residual liquid, or, alternatively, are in solid solution in the same ratio as in the liquid in contact. In either case my estimate of the balanced composition remains unaffected.

The missing link in the scheme among the present papers so far as agreement with what I have said is concerned is in the ingot examined by Dr. Swinden. This contains about 0.047% of carbon, and Dr. Swinden considers that from the fact that when plotted the results go in a clockwise direction this confirms the Hultgren and Phragmén figure. Actually, if Dr. Swinden would take the



lowest-carbon ingot of the three Denain ingots by Mr. Mitchell and plot the figures in the same way as he has done in Fig. 7, he would find that in that case the results go in an anti-clockwise direction as postulated by Hultgren and Phragmén for steel above the balanced composition. The composition there, I think, for carbon was 0.049%, and that is above the true balanced composition. The reason why Dr. Swinden's curve in Fig. 7 takes an anti-clockwise direction is that the steel was initially not saturated to the required value for the Hultgren and Phragmén diagram, namely, an oxygen-carbon product of 0.0025. The product in its outer layers is very much less than that. For some reason there was less oxygen in the system to begin with than was required for the balanced composition or, indeed, for full rimming steel on the basis of the ideas of Hultgren and Phragmén.

There seems to be some confusion as to how to ascertain the carbon content of the residual liquid dealt with by Hultgren and Phragmén. Some people consider that this is the carbon content across the whole core. As a matter of fact, it really is, as near as we can make it, the metal just inside the junction. The remainder of the core, as mentioned by Dr. Binnie and Mr. Mitchell, and, indeed, to some extent the junction too, solidify as a separate entity after the fashion of killed steel within, as Mr. Mitchell puts it, a mould of rimmed material. Incidentally, I think, from gas analysis, that there is some evolution of gas from the core after the rim is formed, and this will reduce—it may be only slightly—the oxygen and carbon contents of the core. A great deal of carbon segregation at least goes into the topmost portion of the core, which, of course, is normally removed before commercial use. It seems to me that to estimate the carbon content of the core one would have to dissolve the entire core, including the segregate and any scum on the top, and make a small allowance for the gas removed.

Coming again to Dr. Binnie's paper, he is, I think, very nearly correct in his estimate of the balanced composition, but I do not think he is correct in his contention that the manganese alters the balanced composition. The facts are against him. In Mr. Mitchell's paper there are at least three different ingots and even more, including the four Corby ingots, which have very high manganese contents from 0.5 to 0.7%, and all these are definitely above the balanced composition.

Dr. A. G. QUARRELL (Sheffield University): My comments are concerned particularly with the hydrogen estimations reported in the various papers, and I am glad to see that Dr. Swinden admits that the hydrogen determinations cannot be regarded as absolute. Actually, I think that, although Dr. Swinden believes the trend of the results to be reliable, it is worth while considering the question of the hydrogen figures in greater detail.



In the case of hydrogen in the metal there are three different ways in which it can be retained: (1) Atomic hydrogen in solution, (2) combined, possibly as hydride, and (3) trapped as molecular hydrogen or methane in pores or small cavities in the metal. In steel the first and the third are the more important possibilities to us. We can concern ourselves with hydrogen in solution and with molecular hydrogen trapped in internal cavities. The value to be attributed to any hydrogen estimations depends upon what one is looking for. If one is concerned with hydrogen in solution it is necessary to prepare the specimen as soon after solidification of the steel as possible and the specimen should be large. We have found that in very small specimens the hydrogen can escape very rapidly and it is not possible to retain anything like a typical hydrogen content. If one is concerned with hydrogen in solution in the steel the standard specimens employed in vacuum fusion give quite useless results. But if one is concerned with molecular hydrogen trapped in cavities then the size of the specimen does not matter, and in the Eighth Report on the Heterogeneity of Steel Ingots<sup>1</sup> Sloman states that in the first three or four weeks after casting, the hydrogen content diminishes, but after that time there is no further change in hydrogen content during a period of many months. He concludes that during those first three or four weeks some of the hydrogen in solid solution escapes into the atmosphere, whilst some becomes stored in internal flaws of various sizes in the steel. It thus remains as molecular hydrogen which cannot escape unless the temperature is raised to a certain extent.

I should like to suggest that if we adopt this interpretation, which is quite in keeping with our own experience in similar matters, we are forced to the conclusion that hydrogen determinations carried out after a considerable length of time should be regarded not as a measure of the hydrogen content of the steel, but rather as a measure of the porosity of the steel—probably on a sub-microscopic scale, but porosity nevertheless. If the hydrogen results be looked at from this point of view, bearing in mind the time which has elapsed between the preparation of the ingot and the sampling, it might be helpful in the interpretation of rimming action.

Dr. C. H. DESCH, F.R.S. (Vice-President; Iron and Steel Industrial Research Council, London): I agree with the other speakers that we have been given very complete data for the testing of the Hultgren and Phragmén hypothesis, which seems now to hold the field. I am going to speak only about one matter. These papers contain a number of photographs of the inclusions and describe the character and behaviour of such inclusions in rimming steel, which may be found to give quite an important clue. With what

<sup>1</sup> *Iron and Steel Institute*, 1939, *Special Report No. 25*, Section VI., Part 2 A.

Professor Andrew said with regard to the diffusion experiments I entirely agree, but Dr. Swinden has brought forward evidence which shows that diffusion over a very short range takes place to a considerable extent. That is shown by the change in the character of the inclusions as the heating proceeds. Therefore I think that detailed examinations across the breadth of an ingot by means of the microscope are very valuable, and it may be worth while to do the same thing with certain other ingots.

Dr. P. M. MACNAIR (Messrs. Richard Thomas & Co., Ltd., Swansea): Mr. Mitchell's reference to the analogy between what is taking place in the rimming action, and the "coming to nature" in the puddling process is interesting. In dealing with the iron-carbon diagram it is more usual to consider what is taking place with falling temperature, *i.e.*, on the vertical axis, but in dealing with rimming steel it is also necessary to consider changes on the horizontal axis, owing to reduction of the carbon content by the formation of carbon monoxide and its escape. The cooling line is not vertical but inclined at an angle towards the origin. If the reaction is going on in the liquid state, I cannot imagine but that diffusion is at least as fast as the rate of carbon elimination. This would keep the metal homogeneous. When the liquid steel begins to set, however, it would appear that the rate of carbon removal exceeds the rate of diffusion, because the rim is purer than the centre. It is true that both changes must be very much slower in the solid than the liquid state. In the puddling process the carbon content of the liquid metal is decreasing at constant temperature, which is below the melting point of pure iron. As the carbon content decreases it reaches the liquidus point corresponding to the temperature, and solid metal of this composition is thrown out as small pellets, which the puddler forms into a ball. Actually this metal contains around 1.0% of carbon. This carbon is finally eliminated to below 0.1% by chemical reaction going on in the solid. If this reaction goes on with a fair degree of rapidity at puddling temperatures, it seems natural to presume that it goes on sufficiently rapidly at steel-setting temperatures to account for the difference in composition between the rim and the core.

Mr. Mitchell has investigated the variation in heterogeneity in 1-, 2-, 3- and 4-ton ingots. Recently we have made a similar ingot in Ebbw Vale, but 8 tons in weight. We are now examining that ingot and it may help to confirm further the various points raised by Mr. Mitchell.

The PRESIDENT (Mr. James Henderson): Will that be a basic Bessemer ingot?

Dr. MACNAIR: Yes, of similar analysis. With reference to Dr. Swinden's paper on the diffusion of carbon across the rim-core

boundary, the persistence of this boundary is noteworthy. Dr. Swinden obtained very little evidence of diffusion. There is a difference in the structure of the steel in an ingot as cast and when rolled or forged, but in rimmed steel the rim persists as a separate structure from the core. I should like to add an observation bearing on this. In rolling sheets we start off with an ingot 25 in. thick, hot-roll it down to about 0.08 in. thick, and finally cold-roll down to 0.02 in. with a final cold-reduction of over 60%. Under such conditions the structure of the steel is badly broken up. However, on annealing, the recrystallised structure shows the persistence of the rim and the core across the section 0.02 in. thick.

Dr. W. C. NEWELL (Brown-Firth Research Laboratories, Sheffield): Dr. Quarrell has introduced the subject of hydrogen in connection with rimming steel, and, while I fail to appreciate the connection, I feel that his remarks call for some response. The loss of hydrogen from small steel samples is a real factor which does limit the significance of hydrogen estimations upon small samples. To attribute the residual hydrogen left a few weeks after casting to gaseous hydrogen present in cavities is, in my opinion, wrong.

Mr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett, Co. Durham): Even in killed or semi-killed ingots the cause of major segregation is difficult to ascertain and is still more so in the case of rimming steels, the distinctive characteristic of which is an outer zone of relatively pure material sharply separated from a very heterogeneous core. How that structure arises cannot at present be stated with any degree of certainty. In the excellent papers under discussion each of the authors has referred to Hultgren and Phragmén's exposition, but, in my opinion, their hypothesis provides no solution to the problem. As far as I am aware, three explanations of that remarkable feature, the rim, have been advanced at different times.

The first was that it was due to the action of the evolving gases, which swept forward the residual mother-liquor into the centre of the ingot. Now it is a striking fact that of the various rimming-steel ingots examined by the Committee Nos. 63 and 64 had the most pronounced rims, and yet the observers reported that a crust began to form as soon as the moulds were filled and that very little gas was liberated during subsequent solidification. I fully believe that to have been the case, for if any appreciable quantity of gas had been evolved, a flame should have been apparent just above the crust at the top, and no mention was made of it. Yet I hesitate to assert that gases are of no consequence in the production of the rim, but think their action can be at most a minor one. The extent to which they are involved may probably be indicated by

the slight decrease in the carbon, sulphur and phosphorus contents of the rim towards the top of the ingot, as shown by Mr. Mitchell, for it seems likely that gas evolution will increase appreciably as the ferrostatic pressure diminishes.

The second explanation ascribed the rim to the deposition of  $\delta$ -iron, so that when the peritectic point was reached in the core the rimming action ceased. The main difficulty in accepting it is that  $\delta$ -iron is also precipitated when 0.2–0.30% carbon steel ingots begin to solidify, and yet their outer zones are quite unlike those of rimming steels.

A third explanation is put forward by Mr. Mitchell in his present paper on rimming steels. It is that the rim results from the deposition of relatively pure iron particles produced by the reaction between the FeO and the carbon. The quantity of iron thus formed is, however, very small; in extreme cases it would scarcely exceed 3 lb. per ton, but Mr. Mitchell believes that the “particles serve as nuclei and carry down with them considerably more iron than their own united weights.” That explanation seems to me to be too far-fetched, and, in the absence of any confirming evidence, I am not prepared to accept it.

Turning now to the paper by Dr. Swinden, in which he claims to have verified Hultgren and Phragmén's hypothesis, the main features of the Fe–C–O equilibrium diagram propounded by those authors is reproduced by Dr. Swinden in Fig. 1; it is based upon the assumption that 0.24% of oxygen can be dissolved in molten iron at the freezing point. In my opinion the solubility of oxygen in iron has not yet been established beyond doubt, but, accepting that figure for the sake of argument, the upper curve  $QP_n$  according to the authors then represents the liquidus of the system and the lower one the solidus. It must be remembered that all the while the rim grows, CO is usually being liberated by the reaction  $\text{FeO} + \text{C} = \text{CO} + \text{Fe}$ , so that four parts of oxygen are escaping to every three parts of carbon. Incidentally, I would point out that, although the reaction is endothermic, its speed seems to increase as the temperature falls, even before the liquidus is reached, which is contrary to Le Chatelier's principle and requires explanation. Now, Hultgren and Phragmén state that at one particular point the liquid will solidify without change in composition and, therefore, at a constant temperature. That balanced composition, as they term it, is maintained by the deposition of solid iron containing just sufficient carbon and oxygen to compensate for the loss entailed by the CO evolution. The same consideration applies also on either side of the balanced composition, but the adjustment at such points is incomplete, so that on the right side, as freezing continues, the liquid will become progressively richer in carbon and to a greater extent poorer in oxygen; on the left the liquid will become poorer in carbon and to a lesser degree richer in oxygen. In making those inferences any possible con-



tamination of the metal with atmospheric oxygen is, of course, ignored.

Changes of a similar nature should likewise occur in the growing solid walls. Thus, when the steel is above the balanced composition, the carbon in the rim should tend to increase and the oxygen to diminish. Below the balanced composition the reverse should happen; indeed, the diagram indicates that the oxygen content of the solid steel should there rise rapidly, notwithstanding any loss as carbon monoxide. The extents to which those progressive changes take place will depend partly on the rate of freezing on the one hand and partly on that of CO liberation on the other. Unfortunately, at present there is no really satisfactory way of obtaining the actual composition of the liquid metal at successive stages of solidification, but that of the solid phase can be determined, as Dr. Swinden has, in fact, done, in four different instances. I have examined those results in order to see how far they comply with the above interpretation of the diagram. Confining attention to the percentages of carbon and oxygen, I found that they changed through the rim in the manner stated in the Table A. In arriving

TABLE A.—*Variations of Carbon and Oxygen Contents.*

Sample No.	Pit Sample Carbon. %.	Carbon Change in Rim. %.	Oxygen Change in Rim. %.
0.16% carbon billet	...	None	...
No. 64	0.06	Drops 0.016	Drops 0.035
H3906	0.047	„ 0.009	„ 0.006
34/8940: Top	0.1	Rises 0.01	„ 0.01
Middle	0.1	„ 0.013	„ 0.009
Bottom	0.1	„ 0.006	„ 0.008

at the figures there given I have disregarded the analyses of the extreme outer parts, both on account of the probable chilling action of the mould and of a possible contamination of the skin of the ingot with mould wash. The 0.16% carbon billet, although it had a characteristic rimming structure, is certainly not in line. Likewise No. 64 is not in agreement, since both the carbon and oxygen contents fall, whereas they should take opposite directions. H3906 is presumably situated below the balanced composition and that steel is also divergent, for, instead of rising, the oxygen in the rim decreases. The only instance in which the carbon and oxygen contents follow the course indicated by the diagram is the 34/8940 sample.

There is another point that I wish to mention in connection with the Hultgren and Phragmén hypothesis. I doubt whether a balanced composition could ever appear in ordinary rimming steels for any length of time, and that for two reasons: The first is that the phosphorus content of the liquid metal steadily increases as the



rim develops, and, since phosphorus lowers the freezing point, solidification at a constant temperature, the criterion of a balanced composition, can never occur, even when carbon and oxygen are present in the right amounts. The second has to do with the sulphur. That element is also largely retained by the liquid. Now, sulphide and oxide of iron are mutually soluble in the molten state, and it seems quite likely, therefore, that, as the liquid becomes richer in sulphur, the amount of oxygen in solution will gradually diminish, owing to absorption by sulphide particles. If so, a balanced composition will not be maintained. That removal of oxygen might also affect the reaction with  $\text{FeO}$ . I think that the effect of sulphur on the rimming action requires a closer examination than it has yet received.

Finally, I would refer to an inference drawn by Principal Edwards in his study of the Hultgren and Phragmén diagram. He emphasised that "a good solid outer wall, or rim, may be found in an ingot which has displayed only comparatively little tendency for the liberation of gas. This might arise when the steel contains a very low percentage of carbon and free, or active, oxygen which places it well within the area  $ABMYN$  of the diagram. In other words, during the earlier stages of solidification it would behave rather like a killed steel."<sup>1</sup> Now I have had but little experience in the manufacture of rimming steels, but it so happens that I witnessed the casting of the Heterogeneity Committee's ingot No. 62, which was well within the field where, according to the above statement, little gas should be evolved at the outset, for the carbon content was 0.03% and the oxygen well above 0.10%, yet the ingot rimmed for at least 20 min. and during the whole of that time a copious volume of gas was evolved.

Dr. W. H. HATFIELD, F.R.S.: While listening to what has been said, I have had recalled to my mind quite a number of outstanding facts which must be brought into consideration in attempting the solution of these problems. Mr. Whiteley has remembered some of them. For instance, there was the case of the rimming steel with 0.2% of oxygen and very low carbon. A very good rim was formed, but very little thicker than an ordinary rim. I think that case provides an anomaly from one or two points of view. I would ask Mr. Robinson whether he actually saw scrap put into the ingot mould in the case that he mentioned.

Mr. ROBINSON: I have seen it done.

Dr. HATFIELD: I should not consider it conclusive evidence unless the ingot was studied without scrap and with scrap. I should also like to point out that the mould is filled with steel and

<sup>1</sup> Ninth Report on the Heterogeneity of Steel Ingots, *Iron and Steel Institute*, 1939, *Special Report No. 27*, p. 9.

then the scrap is put in, but all the time the rim is forming before the putting-in of the scrap. One must be very critical of the mechanism in these operations.

Mr. Whiteley has mentioned  $\delta$ -iron. I have not given up the theory of  $\delta$ -iron as playing a large part in the formation of this rim. The ingot is cast and one arrives at a stage—it can be imagined at all events—at which the rim is formed. But this material which subsequently freezes is the more segregated centre mass. The thought may occur to you that if the rim could be eliminated at this stage and the remaining liquid steel be poured into a cold mould it would still rim. I submit that that is a fact.

The PRESIDENT: Have you any evidence of that?

Dr. HATFIELD: No, I have not; it is really only a theoretical deduction. If a critical examination be made of the material within the rim in one or two ingots it will be realised at once that that material, if caught in a liquid condition and poured into a cold ingot, must necessarily rim. But certainly it does not when it freezes within the rim.

There are two outstanding differences there. One is the temperature of the wall upon which it freezes and the temperature gradient which is possible under these conditions, and the other is the very interesting point brought out by Dr. Macnair relating to this layer of material existing at the junction of the rim with the interior. I feel that there we have two factors to consider. We have the modification of the liquid layers adjoining the rim on the one hand and the entirely dissimilar temperature gradient on the other, and neither of these factors is taken into account in the Hultgren and Phragmén theory.

I must remind Dr. Swinden about the Denain ingot, the original one, which had a very thick rim on the top, and from which, we were advised, very little gas came off. Indeed, such gas could not have come off, owing to the very nature of the upper surface. That is a third reason for the view that this reaction is not essential to the production of the rim.

There is another very important factor which is often overlooked, bearing on the gases which come off steel. We have, for example, a steel supercharged at, say, 30°, 40° or 60° C.; there is a higher gas content at these relatively elevated temperatures, and between such temperatures and that of freezing large quantities of gas may come off. One can very easily confuse such evolution of gases with reaction gases.

My own desire has been just to keep this subject open and to point out that there are quite a number of anomalous facts which must be considered properly before we can expect to agree on the question of rimming.

Dr. T. SWINDEN (Member of Council; The United Steel Companies, Ltd., Stocksbridge, near Sheffield): Referring to the first paper read by Mr. Mitchell, the comparative study of the three Denain ingots, Mr. Mitchell accepts, quite properly, the report of the observers that ingot No. 64 did not show any gas being given off. That has been referred to repeatedly. I hesitate to say that it was a faulty observation, but I should like to differentiate between free effervescence and the giving off of gas. I should say that gas was given off, because there was a rim, and I consider that the rim was produced through the reaction between  $\text{FeO}$  and carbon, and therefore  $\text{CO}$  was given off.

Dr. Binnie's paper is particularly interesting. I have already been in correspondence with him with regard to samples from this ingot, because it is very important that we should check up the oxygen figures. In some particulars the ingot which he has described is quite extraordinary. It is extraordinary to have a pit sample of 0.08% carbon, and yet in the position just *inside* the core to have the carbon down to 0.015% as in position *F5*, Table I. Further, the carbon, after going up only to 0.035%, continues to decline as we traverse through the core. That is something which demands further investigation.

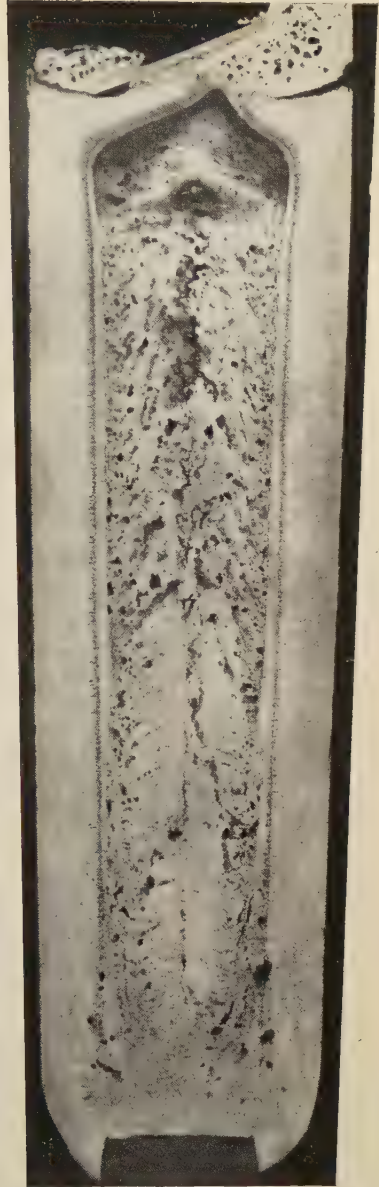
I have also had checked up the carbon-oxygen ratios and the carbon variations for such data as we possess, and, despite the criticism of Dr. Dickie, which one much appreciates, on the figure suggested by Hultgren and Phragmén, I still think that their figure is perhaps not very far from what they intended to represent. It is not a matter of swallowing a theory from Sweden. Hultgren and Phragmén did put into very cogent language a theory of the production of the rim and of the changes in composition from the rim to the core. The work which we have done has been directed to seeing whether in fact the data fall in line with that hypothesis or not. In my opinion, they do.

Finally, we have Mr. Mitchell's report on the four Bessemer ingots. This might be regarded as the first of a series of practical papers. The influence of size of ingot with a given cast of steel was investigated. Obviously there were other variables which required to be studied in just the same way, and I hope the future work will be of this type.

There is a point in Mr. Mitchell's paper upon which I should like him to comment. He has stressed the three really important things in commercial rimming steel, and the only point I want to make is that he—and I think also Dr. Dickie—has rather discounted the effects of pressure. If one accepts the theory that rimming goes on in consequence of the reaction  $\text{FeO} + \text{C} \rightarrow \text{CO}$ , it is obvious that the  $\text{CO}$  pressure must be important. I have a very interesting example which was provided from the same cast, *H3906*, as the ingot dealt with in my paper to this Meeting. This ingot (No. 3 in the order of casting) rimmed normally for some 15 min. and then



(a) Sulphur Print.



(b) Macro-Etching.

FIG. A.—Cast H3906, Ingot No. 3. (See Swinden's verbal contribution.)

[Discussion on Rimming Steel.  
[To face p. 376 p.]





suddenly spurted some metal from the nearly solid top. It was plated down and subsequently sectioned. The results are shown in Fig. A. The interesting point is that the thickness of the original rim is the same in both ingots, but, with *the release of pressure* when No. 3 ingot spurted, rimming was resumed.

This, I think, provides adequate proof that ferrostatic pressure, together with the actual pressure of the CO gas produced, is important in controlling the rim depth.

### JOINT CORRESPONDENCE.

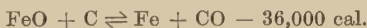
Mr. W. L. KERLIE (Messrs. Stewarts and Lloyds, Ltd., Corby) wrote: The report by Mr. Mitchell on four ingots of basic Bessemer steel may well be regarded as an important contribution to the underlying technique of rimming steel manufacture.

Figs. 2 to 10 inclusive are of particular interest, and an examination of these has helped considerably in explaining the variation in the shape of the ingot top and the influence of aluminium additions on the rimming action generally. The distribution of the blow-holes in the four ingots examined indicated, as the author has stated, the importance of the gas bubbles and currents in the molten metal in determining the character of the rim. I feel, however, that the ferrostatic pressure is equally effective in determining the distribution of the blow-holes generally.

During the normal rimming action, the velocity,  $V$ ,<sup>1</sup> is given by:

$$V = K_1 [\text{FeO}] \cdot [\text{C}] - K_2 \cdot p_{\text{CO}},$$

where  $K_1$  and  $K_2$  are constants and together compose the equilibrium constant  $K$  for the reaction:



By integrating the Arrhenius equation, and by the use of the mass-action law:

$$\text{Log } K = -\frac{Q}{RT} + C = \text{log } \frac{p_{\text{CO}}}{[\text{FeO}] \cdot [\text{C}]},$$

where  $Q$  is the heat absorbed during the forward reaction, and in this case is positive. This means that with increasing temperature the value of  $K$  will increase by virtue of the decrease in  $Q/RT$ . Thus  $p_{\text{CO}}$  will tend to increase with respect to the  $[\text{FeO}] \cdot [\text{C}]$  product and the velocity of the reaction will decrease, and, conversely, with decreasing temperature the reaction velocity will tend

<sup>1</sup>  $V$  may be represented by  $dc/dt$ , the rate of carbon removal, and when this is zero:

$$K_1/K_2 = P_{\text{CO}}/[\text{FeO}] \cdot [\text{C}] = K.$$

to increase, the stipulations being for dilute solutions where the energy  $Q$  is more or less constant and is small compared with the total available energy, in this case the latent heat of solidification and the superheat in the liquid metal.

On this reasoning the value  $p_{CO}$  during the reaction will increase, owing to ferrostatic pressure, towards the bottom of the ingot, which means that the velocity of the reaction decreases with increasing depth in the ingot. Thus the change in composition in the rim will be more marked the higher the position in the ingot, bearing in mind that the velocity of the reaction is not necessarily a function of the rate of solidification, and these two terms should not be confused. This is borne out by the analyses in Table II. and particularly by the carbon and oxygen figures of samples *T2*, *M2* and *B2* :

No.	4 Ton.		3 Ton.		2 Ton.		1 Ton.	
	Carbon. %.	Oxygen. %.	Carbon. %.	Oxygen. %.	Carbon. %.	Oxygen. %.	Carbon. %.	Oxygen. %.
<i>T2</i>	0.039	0.012	0.036	0.011	0.041	0.010	0.047	0.020
<i>M2</i>	0.041	0.016	0.042	0.016	0.046	0.017	0.052	0.022
<i>B2</i>	0.043	0.025	0.051	0.026	0.047	0.023	0.064	0.028

From these figures it is evident that the reaction  $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$  has decreased in velocity towards the bottom of the ingot in each case. Again, although the results are not quite so definite, there is a decided trend showing an increase in carbon and oxygen, and hence a decrease in the velocity of the reaction, with the smaller ingots.

Further evidence in support of this contention may lie in the fact that, in the extreme bottom, the lenticular blow-holes are shorter, more numerous and more removed the greater the ingot size, indicating that the bubbles of CO escape more readily in the larger ingots, because of the greater velocity of reaction with respect to speed of solidification, or "specific reaction velocity" if I may be allowed to coin this phrase.

Turning to the question of blow-hole formation, the sketches in Figs. B and C should serve to illustrate my remarks.

Fig. B(a) represents the development of the normal rimming action after the formation of the outer chilled crystal zone. The formation of CO bubbles throughout the length of the solidifying wall causes the liquid surface to rise somewhat in the mould, but a short time later, when the normal rimming action has proceeded and which can be induced by the addition of a few pellets of aluminium, the circulation of the metal facilitates the removal of the gas bubbles in the upper portion of the ingot. At the extreme bottom of the ingot the rimming action is more sluggish and the gas bubbles move comparatively slowly towards the centre.

The stage represented by Fig. B(b) has now been reached, and here the vigorous circulation of the metal is confined to the top half of the ingot because of the increasing specific reaction velocity

towards the top. Owing to the freeing of suspended gas bubbles in the top half of the ingot the metal surface tends to sink again, but towards the bottom the tendency for the gas bubbles to remain suspended still persists.

In Fig. B(c) the blow-holes in the lower half of the ingot have become fixed and the rapid circulation of the metal is confined still further to the top. The rate of solidification is reduced because of the thickness of the ingot wall, and the condition is essentially isothermal. For this reason the specific reaction velocity is increased and the gas bubbles escape readily with a further drop in the  $[C] \cdot [O]$  product. In all probability the lenticular blow-holes in the lower half of the ingot provide an insulation against heat removal, and further blow-hole formation in this region is avoided except at the lower extremity.

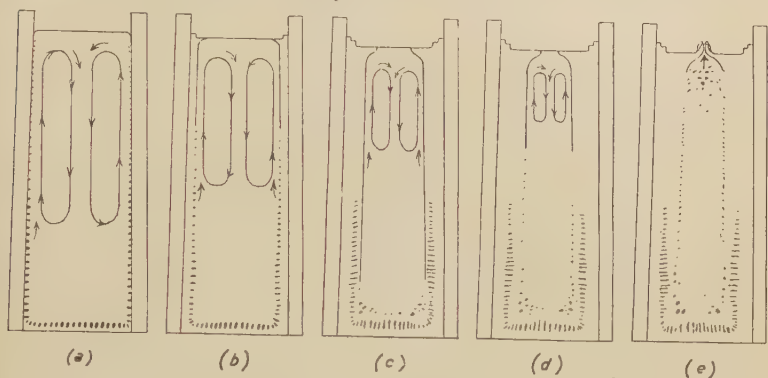


FIG. B.—Development of Normal Rimming Action.

In Fig. B(d) the metal circulation at the top tends to be erratic, and as the rimming action is nearing completion and coinciding with the definition of the rim-core junction, blow-holes are formed throughout this junction and particularly towards the bottom.

The final solidification of the ingot top is taking place in Fig. B(e) and an erratic emission of liquid metal builds up a small cone on the top surface with the formation of gas bubbles in the core.

By reference to Fig C, the formation of the lenticular blow-holes in a large ingot and small ingot can be explained in much the same way.

Reverting to Fig. B, it is considered that, during the rapid formation of the outer chilled zone, differential solidification has not occurred and the concentration of  $FeO$  is too low to permit of any reaction. Later the rapid development of the dendrites tends to trap the enriched liquid and suspend the reaction. The lowering temperature, however, increases the rate of the  $FeO + C$  reaction sufficiently to disrupt the dendritic form and allow the  $CO$  to escape.

With a hot cast this stage is marked by the metal rising in the mould, and this is considered to be due to the high-temperature conditions slowing the rate of the  $\text{FeO} + \text{C}$  reaction and causing the bubbles of  $\text{CO}$  to be temporarily suspended on the growing surface of dendrites.

As the rimming action proceeds the rate of solidification is progressively reduced, owing to the decreasing temperature gradient,

and the  $\text{FeO} + \text{C}$  reaction proceeds freely, the temperature of the liquid mass decreasing owing to the circulation of colder metal from the top of the ingot. The reaction towards the bottom is, however, still fairly slow, owing to the ferrostatic pressure and the hotter metal in this region.

As a consequence the carbon and oxygen contents in the rimmed portion are lowered progressively during the rim formation, and the minimum content of these elements is reached at the rim/core junction, where the  $\text{FeO} + \text{C}$  reaction ceases suddenly, owing to the cap sealing over and the  $\text{CO}$  pressure building up. In all probability the viscosity of the liquid metal at this stage is high, owing to suspended crystals and the cooling effect of the circulating

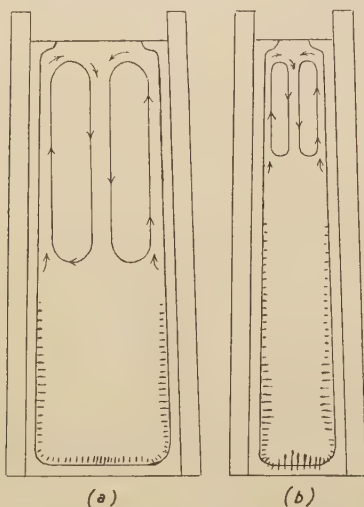


FIG. C.—Formation of Lenticular Blow-Holes in Large and Small Ingots.

metal over a period which has now approached something like 20–25 min.

Hence it may be reasonably inferred that, with the smaller-sized ingots especially, complete solidification of the core may require only a few more minutes. This may explain the presence of blow-holes in the core of all four ingots; and the particularly large number of blow-holes in the core of the smallest ingot may be due to the intermittent ejection of the viscous metal at the top.

In the light of this hypothesis it would seem that the ferrostatic pressure, which is approximately 15 lb. per sq. in. at the extreme bottom of the ingot, is a major factor in determining the structure of the ingot.

Dr. T. SWINDEN (Member of Council; The United Steel Companies, Ltd., Stocksbridge, near Sheffield), referring to Mr. Mitchell's paper on four basic Bessemer steel ingots, wrote: It is important to note the last sentence on p. 328 P of the steelmaking data, wherein it is stated that an extra  $\frac{1}{4}$  oz. of aluminium was added to the top



of each ingot after the mould was full. Without wishing for a moment to detract from this excellent piece of work, it is felt that this has had an important bearing on the behaviour of the tops of these ingots. Thus, I was surprised to read, in the middle of p. 343 P, that in the author's opinion, in the case under review, *less* aluminium should have been added to the 3- and 4-ton ingots and rather *more* to the 1-ton ingot. As a matter of practical experience, one would have thought that the reverse should obtain as regards the general use of aluminium as distinct from the addition of aluminium for the purpose of setting the top. Thus, it is, of course, common practice that, if one experienced the tendency to "sink" evidenced by the 4-ton ingot, a little more aluminium would be added to ensure a satisfactory rimmed ingot.

This has a rather important bearing on the statement that for the same metal more aluminium will be required with small than with large ingots.

I would reiterate that Mr. Mitchell has drawn attention to the three essential factors that determine the nature of rimming-steel ingots, namely, the thickness of the rim, the lenticular blow-holes in the lower portion (with particular reference to the thickness of the skin protecting these blow-holes) and the incidence of blow-holes and non-metallic inclusions at the rim-core junction. I consider that Mr. Mitchell has presented a very sound and practical treatise on the subject.

In introducing the paper, the author raised the question of why it was possible to produce satisfactory rimming steel in the basic Bessemer with an iron content of the slag of the order of 8–10%, whereas in basic open-hearth practice it was necessary to have a slag containing nearly 50% more iron. Dr. Macnair's suggestion to the effect that more iron was present as  $\text{Fe}_2\text{O}_3$  in the open-hearth slag is no doubt an important contributory factor, but it is surely to be explained by the fact that in the Bessemer process oxidation of the metal occurs by direct reaction between the iron and the oxygen of the blast. In the basic open-hearth furnace the oxygen content of the metal is controlled by slag-metal reactions and, except under conditions of very low carbon and/or pronounced over-oreing, a condition approaching equilibrium should be achieved.

In the Ninth Report of the Ingot Committee<sup>1</sup> (see Fig. 36) Mr. Cawley and I presented a note on acid Bessemer practice, showing how steeply the oxygen content of the metal rises while the carbon is still comparatively high. Wentrup<sup>2</sup> also shows how, in the acid Bessemer process, the carbon always hangs back and a higher oxygen content in the iron than equilibrium conditions would call for is required.

Mr. Mitchell made the suggestion that in the Bessemer process the oxygen might be dispersed more intimately, but I would

<sup>1</sup> *Iron and Steel Institute*, 1939, *Special Report*, No. 25.

<sup>2</sup> *Stahl und Eisen*, 1942, vol. 62, pp. 749–756.



suggest that the oxygen is essentially in solution in the liquid steel in both processes and is only thrown out of solution when the steel cools down and particularly on freezing.

As will be noted from Mr. Mitchell's paper, the oxygen content of his basic Bessemer steel at position *M1* (*i.e.*, the outer edge of the rim at the middle of the ingot) is of the order of 0.041–0.043%, whereas in a similar position in ingot *H3906*, an ingot of basic open-hearth steel of slightly lower carbon content, dealt with in my paper (p. 345 P), the oxygen content is only 0.020%.

Mr. W. ASH (Messrs. Steel, Peech and Tozer, Sheffield) wrote : The control of rimming steel by additions of aluminium in small amounts, as described by Mr. Mitchell, can be very effective. One assumes that the amount of aluminium used is varied according to the behaviour of the steel during casting.

In our experience the amount of aluminium required varies inversely with the carbon and manganese content of the steel. It has been found quite practicable in basic open-hearth steel practice to make the addition of aluminium to the ladle, on the basis of the carbon and manganese expected in the steel.

Observation of rimming steels during casting shows that the strength and character of the effervescence varies widely. Very low-carbon steels sometimes exhibit little or no tendency to give up gas until several minutes have elapsed, presumably until sufficient heat has been lost. Occasionally, of course, an off-grade cast is tapped which develops only a weak effervescence. In this case the level of liquid steel in the mould will continue to rise steadily but rapidly after teeming is finished, indicating extensive blow-holes adjacent to the ingot surface instead of at the usual depth. Aluminium in small quantities will only aggravate this condition; what such casts really need is a dose of oxygen.

There appears to be some controversy over the upper carbon and manganese limits of rimming steel. No doubt these are not the same for all steelmaking processes. In fixed-furnace basic open-hearth practice it has been found that the upper limits are approximately 0.25% of carbon with 0.60% of manganese. Admittedly the better examples are to be found in the lower ranges, but in the higher ranges a regulation rim and core structure is to be found just the same.

Dr. HUGH O'NEILL (London, Midland and Scottish Railway Company Research Laboratory, Derby), referring to Dr. Swinden's paper on the composition variation of rimming steel from outside to centre, wrote : Studies of the properties of rimming steels may well be of value outside the field of structural-steel production. The possible application of the data obtained in the present paper to the behaviour of certain types of steel weld-metal should not be overlooked. In particular, the effects of hydrogen content may be

of interest in connection with the view that metallic-arc weld beads possess inferior properties if their hydrogen content is high. An effect looking something like rimming has been observed in the macrostructure of the "ingot" inside large spot welds in steel. Similarly, blow-holes have been developed within a single steel plate subjected to spot-weld electrical heating.

The Hultgren-Phragmén hypothesis that a mutual-removal reaction occurred between dissolved carbon and oxygen in liquid rimming steel is of interest to me, because of some experiments on reactions in the solid state described in the *Journal* for 1929.<sup>1</sup> These were made with solid "ingot iron," which might be looked upon as consisting of all-rim metal, and the mean carbon content was about 0.04% in the specimen used. A bar of this iron was normalised in air at 900° C. to remove all hardening effects, and a small piece was then annealed in an X-ray vacuum at a temperature of about 750° C. for 4 hr. and cooled *in vacuo*. Careful hardness measurements were made before and after vacuum-annealing, and it was surprising to find that the hardness had been reduced about 20% by the latter process. It was concluded that there had been reaction between carbon and oxygen in the solid steel, and that the resulting gaseous products had been removed from the system because of the reduced pressure on the outside.

At the time of the experiments I formed the opinion that the ferrite grain size and the  $\alpha$ -veining of this ingot iron were associated in some way with the oxygen content of the material. The general relation between ferrite grain size and Brinell number, for instance, is known to be confused, and conflicting results have been obtained by different workers. Finally it has been found that if steel completely decarburised in hydrogen is used for hardness experiments, then the indentation values are quite independent of the ferrite crystal size. These observations made the author's Fig. 9 of particular interest, for macro-etching showed that the rim of the ingot had a fine crystal size, whilst the core was relatively coarse. Has the author examined the ferrite crystal size from skin to core of the ingot? If so, did the size change in any regular way which could be associated with the oxygen content of the steel at the same position?

Dr. H. LEE (Sheffield University), referring to Dr. Swinden's paper on the composition variation of rimming steel from outside to centre, wrote: The author is to be congratulated on adding valuable data to the verification of the hypothesis on rimming action postulated by Hultgren and Phragmén. The steel employed by the author was almost identical in composition with the ingot *G* reported in Hultgren and Phragmén's work, and it is interesting to note that, although one ingot was about five times as heavy as the

<sup>1</sup> O'Neill, *Journal of The Iron and Steel Institute*, 1929, No. II., p. 207.

other, the agreement in the distribution of the carbon, oxygen, sulphur and phosphorus was certainly most remarkable.

I am particularly interested in the variation of hydrogen across the ingot shown in Fig. 6. Here the author is quite right in pointing out that, in the light of the time effect, sample preparation and method of determination, the hydrogen value cannot be regarded as absolute. In my opinion, even the trend of the curve cannot be accepted as representative if it is intended for the ingot immediately after solidification. In view of the fact that the ingot had been left for some time before examination, it is not surprising that the reported hydrogen value is very low throughout. The peak on the hydrogen curve corresponding to the rim-core junction could easily be due to the presence of blow-holes into which hydrogen had diffused and become stored there.

Referring to cast 34/8940, am I right in saying that probably the time elapsed before the sample was taken was not very long, and therefore a much higher hydrogen value was obtained? It may be recalled that this ingot was rolled to close the blow-holes, and the gradual increase of the hydrogen figure towards the centre is precisely what would be expected from a solid and relatively freshly cast sample.

The author said that the lower hydrogen value obtained in cast H3906 was not unexpected in view of its higher oxygen content. Does this mean that, owing to the presence of the relatively large amount of oxides in the steel, the hydrogen analysis is in error, or does it imply that a low hydrogen content is characteristic of steel having a higher oxygen content? It is generally claimed that rimming steel tends to be low in hydrogen because of its long boil; was there any difference between the boiling period of the two casts in question?

Whether the difference in hydrogen content between the two casts was due to any single factor or to all factors involved, the importance cannot be denied, and any enlightenment on the subject will be welcomed by those who are engaged on work in this direction.

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### AUTHORS' REPLIES.

Dr. BINNIE wrote in reply: The carbon content at the balanced composition was the subject of some dispute. Dr. Swinden held to the 0.06% of carbon figure and Dr. Dickie was more inclined to a figure of about 0.04% of carbon. It must be remembered that the balanced composition is taken to be the highest point of the curve of intersection of the  $\delta$  liquidus plane and the hyperbolic surface of the carbon-oxygen product. The highest point of the curve when the composition is constant varies with change of pressure, and only at the very top of an ingot can the pressure be considered to be about

1 atm. At the bottom of a 6-ft. ingot the pressure would be at least fully 2 atm., and the balanced composition is affected accordingly.

Dr. Dickie remarked that manganese did not affect the balanced composition, but additions of manganese altered the tilt of the  $\delta$  liquidus plane and, incidentally, the highest point of the curve of intersection of the two surfaces, *i.e.*, the balanced composition. There is no one balanced composition to cover all rimming steels. The balanced composition depends on the composition of the steel and the pressure, and is affected by the amount of manganese present or by the presence of any other additional elements. One way of showing the balanced composition is to plot  $(45 - z)$ , the temperature depression, against  $x$ , the carbon content, in equation (3), p. 291 P. Curves for 1 atm. and for 2 atm. are drawn in Fig. D. They

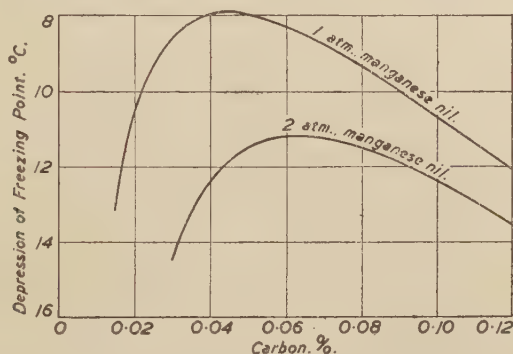


FIG. D.—Balanced Composition at Maxima on Curves.

show the temperature at which the carbon-oxygen product surface cuts the  $\delta$  liquidus plane; for carbon contents lower than or higher than the balanced composition the liquidus curve is towards lower carbon or towards higher carbon values, respectively.

Dr. Dickie cited the three Denain ingots and also the four ingots of basic Bessemer steel reported on by Mr. Mitchell to support his argument about a fixed balanced composition. All these ingots should be theoretically below the balanced composition, yet all of them were, as regards carbon analysis, above the balanced composition.

However, examining the four ingots of basic Bessemer steel, the pit carbon analyses of these four ingots are given as 0.053–0.056%. These ingots on freezing effervesced to a greater or less degree and would give off a gas, mainly carbon monoxide. Thus, the ingot analysed as a whole, regardless of whether the steel composition was above or below the balanced composition, must contain less carbon than the pit sample, say, something like 0.045–0.050% of carbon at the most. Therefore the analysis taken over cross-sections throughout the ingot should have produced figures which, when averaged,



allowing for the area effect, gave a total integrated analysis of 0.045–0.050% of carbon. The analyses recorded in Table II. of the paper on the four ingots of basic Bessemer steel suggest a much higher integrated figure than this. The outstanding instance is the bottom positions of the 1-ton ingot, which are reported as 0.070%, 0.064%, 0.076% and 0.065% of carbon. All these figures correspond to a pit sample with 0.053% of carbon. Contamination by mould wash might be responsible for the outer-edge figure of 0.070% of carbon, but, nevertheless, it is more than probable that the pit-sample carbons reported are distinctly low. Deductions drawn from the carbon contents of the pit samples of these ingots are open to question. Deductions from the carbon contents of the pit samples of the Denain ingots are similarly open to question.

In reply to Dr. Swinden about the carbon analysis of the ingot, I would remind him that this ingot differs from the others examined in that no aluminium addition was made to control the rimming action. The steel was allowed to effervesce freely, the object being to permit of the study of the rimming action in perhaps its simplest form. However, the ingot in question has now been forwarded to Dr. Swinden for oxygen determinations, and, no doubt, he will make use of the opportunity to examine the carbon analyses at the *F* positions.

Mr. MITCHELL wrote in reply: I wish to thank all those who contributed to the discussion of the two papers under my name. The papers themselves were an effort to summarise a considerable mass of data and the various comments which they have called forth can be regarded as supplementary to my own contributions. From this standpoint, perhaps, no reply is necessary to the various points which have been raised, but some further notes may be appreciated.

Mr. Robinson's thoughtful contribution mentions two points of considerable importance. I agree that from the users' point of view Denain ingot No. 64 was probably a satisfactory piece of material, although in its preparation it did not appear to conform to what has come to be regarded as standard rimming practice. On the other hand, it does not seem likely that an ingot of this particular type could be duplicated regularly from blow to blow as a matter of standard works practice. I also agree that information from the user as to the particular carbon content of the core which gives best results in any given process of manipulation is desirable.

Dr. Dickie's remarks are in line with my own views. To some extent I regard the balanced composition as being of little more than academic interest, but I consider, as indicated in the papers, that the Hultgen and Phragmén figure of 0.06% of carbon is too high. The point made by Dr. Dickie regarding the carbon-oxygen ratio, noting the similarity outside and inside the junction and the very considerable variation from ingot to ingot, is well worth



putting on record, and I agree with his conclusion that any carbon and oxygen present in the rim arise from trapped residual liquid.

Dr. Macnair's interesting remarks would of themselves justify my suggestion of an analogy between the rimming action and the later stages of the puddling process, although I am not prepared to agree that in the puddling process "the carbon content of the liquid metal is decreasing at constant temperature." From my own practical observations I know that in this process the temperature is rising steadily towards the end, although it never attains the melting point of pure iron. The point in my mind when writing the paper was that there was a physical resemblance between the two processes, although the reaction itself was taking place under conditions of falling temperature.

I note that Mr. Whiteley is not prepared to accept the explanation given for the formation of the rim and that neither does he consider that earlier explanations are acceptable. In the section of the second paper dealing with my own views as to the rimming action, I suggested that the rim formation might be the result of a complex series of physical changes in which all of the explanations summarised by Mr. Whiteley might play a part. Whilst it is very useful to summarise the various explanations as separate and individual processes, and whilst it is perhaps even permissible to turn each one down as *the* explanation, this surely does not preclude the possibility that each one may play some part in the complete process.

In future studies of the formation and properties of the core portion, Mr. Whiteley's remarks on sulphide and oxide of iron are worthy of full consideration. It would be interesting to know how far the sulphide content of the core, because of its effect on the FeO present, controls the duration of the later stages of the rimming action itself.

I am particularly grateful to Dr. Swinden for his valuable contribution on the paper on the four basic Bessemer ingots. I do not discount the effects of pressure on the gas-evolution reaction. I agree with the explanation given on the interesting prints (Fig. A), *i.e.*, that rimming was resumed when the pressure was released. This section certainly supports the view that rim formation does require contemporaneous evolution of gas. One hesitates to suggest further work to Dr. Swinden, who has already done so much in this particular sphere of investigation, but an analysis of the thin rim inside the junction holes shown in Fig. A might provide useful information as to the reactions which went to its formation. On the subject of aluminium additions, my view is that, in the case of the four ingots under review, the continuance of effervescence in the two larger ingots would have been possible right up to the moment of solidification if the available oxygen had not been fixed by too large an addition of aluminium, whilst in the case of the 1-ton ingot more aluminium would have brought the

rimming action into line with the physical changes of freezing and thus avoided the eruption which took place towards the end of solidification in this particular sample. I agree with the distinction drawn between the use of aluminium for control purposes and for setting the top.

I consider Mr. Kerlie's contribution a valuable amplification of the ideas outlined in the second paper. It is doubtful, however, whether the depth to which the circulating current goes is foreshortened in the way indicated in Mr. Kerlie's sketches (Figs. B and C). I consider that the current of metal traverses the whole liquid depth of the core right up to the moment of final solidification, although in the case of small ingots there is probably considerable interference with this movement, especially towards the bottom.

I agree with the comments made by Mr. Ash on the use of aluminium as a controlling addition in the rimming process and am grateful to him for bringing out the significance of carbon and manganese in this connection. The reluctance of very low-carbon heats to commence gas evolution to which Mr. Ash refers may be due either to high temperature or alternatively to an inherently weak effervescence. The suggestion that what these casts really need is "a dose of oxygen" is quite definitely correct.

Whilst the general trend of the discussion may have left the impression that the rimming process is one demanding great accuracy so far as composition and physical reactions are concerned, it may be desirable in conclusion to point out that there are wide operating margins within which a good commercial product may be made when producing ingots of rimmed steel.

Dr. SWINDEN wrote in reply: I have noted with interest the suggestion made by Professor Andrew in explanation of the curves for carbon contained in the paper on diffusion. A very thorough re-examination of the treated sample does not provide any evidence of unsoundness or formation of cavities. All the dark areas illustrated in Fig. 10 are, in fact, pearlitic. A further endeavour has been made to check the carbon determinations by careful micro-examination, from which it is concluded that there is a slight but definite diffusion of carbon in the rim towards the outside. The increase in carbon across the rim-core junction zone is more gradual in the treated than in the untreated sample. It is, of course, agreed that the rate of diffusion in such a dilute solution would be comparatively low, but it is suggested that the concentration of sulphur and phosphorus commonly found in the vicinity of the junction has a retarding effect on diffusion.

In this connection, Dr. Macnair's contribution is noted and his observation is fully confirmed. No amount of reheating and rolling down appears to break down the boundary between the core and rim originally present in the cast ingot.

I appreciate very much the thoughtful contribution from Dr.

Dickie, and note his suggestion that cast H3906 was not initially saturated with oxygen to the required value for the Hultgren-Phragmén diagram. I can only reply that the cast was given all the ore that it required to produce what I consider to be a very satisfactory rimming-steel ingot of this type. As in the case of Example 65 in the Sixth Ingot Report, of which it is a counterpart, this cast had an addition of 50 lb. of aluminium (to a 75-ton cast) in the ladle. I quite realise the difficulty of computing the balanced composition from the analyses of samples taken from the resulting ingot. Further work is being done by sampling a considerable number of rimming-steel casts, by taking rapidly-killed pit samples and analysing carefully for carbon and oxygen.

It is well recognised that the precise figures for the balanced composition require considerable elaboration. All that I have endeavoured to do in the present contribution is to illustrate in some detail a case where a carbon-oxygen curve goes in a clockwise direction, as postulated by Hultgren and Phragmén.

I do not propose to cross swords with Dr. Quarrell on the subject of hydrogen. It has been well recognised (and in fact data have been published) that hydrogen results cannot be accepted as representing the hydrogen content of the steel as cast if small samples are cut for test from the resulting steel, and particularly if some time is allowed to elapse before the hydrogen determination is made. I think we have insufficient evidence here to confirm or contradict the suggestion that the whole of the hydrogen reported in Fig. 6 has in fact occurred in internal cavities, even recognising that these may be on a sub-microscopic scale. I agree with Dr. Newell in questioning this as a complete statement.

Mr. Whiteley, in a characteristically thoughtful contribution, raises doubts about the soundness of the Hultgren and Phragmén hypothesis. May I, in the first place, deal with his point that as the  $\text{FeO} + \text{C}$  reaction is endothermic, its speed should decrease with decreasing temperature, according to Le Chatelier's principle. I would refer him to the contribution by Dr. Gregory in the discussion on the Sixth Report,<sup>1</sup> in which he pointed out the probability that the latent heat of fusion would have an important bearing in reversing the direction of this reaction during solidification. It is a point to which insufficient attention has been given.

I think perhaps there is still a little misconception as to what is really conveyed in Fig. 1 and illustrated from data in Figs. 2 and 7. In order to make this point clear, I have set out the two corresponding curves in a composite diagram, Fig. E. I have really nothing to add beyond reiterating that, in my view, these curves do provide support for the diagrammatic representation of the carbon-oxygen variation, through the rim and into the core of rimming steel, as postulated in Fig. 1.

<sup>1</sup> *Iron and Steel Institute, 1936, Special Report No. 9A, p. 8.*

I appreciate very fully the admirable contribution from Mr. Kerlie.

Dr. O'Neill's interesting contribution is carefully noted. Unfortunately, pressure of other work has prevented a careful examination of the point that he raises, but I imagine that there would be some difficulty in attributing differences in ferrite crystal size entirely to oxygen content, in view of the differences in the contents of other constituents at the same time.

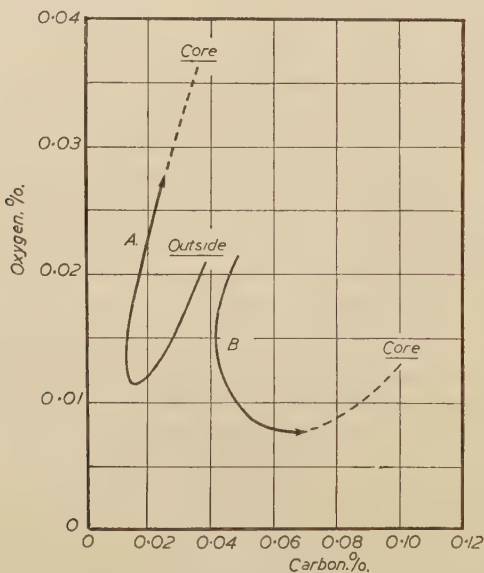


FIG. E.—Composite Diagram of the Carbon-Oxygen Variation across the Rim Zone of Rimming Steel respectively below and above the balanced composition. A.—Cast H3906; carbon 0.047%, manganese 0.10%. B.—Cast 34/8940; carbon 0.10%, manganese 0.31%. The arrows indicate the direction from outside to centre and the continuous lines mark the extent of the rim-zone samples examined.

Finally, I thank Dr. Lee for drawing attention to the agreement in results between those now published and ingot *G* reported by Hultgren and Phragmén. Knowing something of Dr. Lee's own work on hydrogen, I appreciate his comments on this subject.

As previously stated in reply to Dr. Quarrell, it may be that even the trend of the curve for hydrogen cannot be accepted as representative of the ingot immediately after solidification. I feel that we require to reserve judgement on this point.

Dr. Lee is correct in his surmise that the time elapsing between casting and examination of the ingot from H3906 was longer than

in the case of cast 34/8940, and, further, it will be remembered that the latter was examined in the bloom form.

The comment that the lower hydrogen value obtained in cast *H*3906 was not unexpected in view of the higher oxygen content was intended to imply that a low hydrogen content is characteristic of steel having a high oxygen content. The boiling period for cast *H*3906 was longer than that of cast 34/8940, and I agree that on these grounds alone a lower hydrogen content might be expected in the steel.

It was not within the scope of this paper to deal adequately with the subject of hydrogen. Whether, as has again recently been suggested in American literature, hydrogen plays any important part in the rimming reaction, and particularly has any importance in controlling the occurrence of skin blow-holes, must await further experimental data.





# SECOND REPORT OF THE MOULDING MATERIALS SUB-COMMITTEE OF THE STEEL CASTINGS RESEARCH COMMITTEE.<sup>1</sup>

(Figs. 3 to 5 = Plate XXXVIII.)  
(Fig. 12 = Plate XXXIX.)

*Paper No. 3/1942 of the Steel Castings Research Committee  
(submitted by the Moulding Materials Sub-Committee).*

## SECTION I.—INTRODUCTION AND SUMMARY.

SINCE the publication of the First Report of the Moulding Materials Sub-Committee,<sup>2</sup> an important part of their work has been the investigation of possible alternatives to bentonite for the bonding and revivifying of moulding and core sands. The fundamental investigation of the characteristics of bond clays and of the mechanism of bonding which is in progress has already confirmed the superior bonding of clays of the montmorillonite type. Apart from the fullers' earths the only clays occurring in Great Britain so far found to be rich in minerals of the montmorillonite group are those occurring in the London Clay measures, but they also contain a high proportion of siliceous silt which lowers their bonding power. The bond strength, the ratio of dry strength to green strength and the range of retention of green strength with increasing moisture content of clays, &c., containing montmorillonite clay substance has been shown to be almost directly as their montmorillonite content.

With the collaboration of The Fullers' Earth Union, Ltd., selected and treated varieties of fullers' earth, occurring in Somerset and Surrey, to which the general designation of Fulbond has been given, and which have bonding characteristics close to those of normal bentonites, have been developed. Following exhaustive laboratory tests and foundry trials, the attention of foundries was directed to this suitable alternative to bentonite; in most foundries a marked degree of success has attended its use, and bentonite has either been eliminated or its consumption very considerably reduced. A large tonnage of Fulbond is now being used in foundries and this usage is likely to continue even when bentonite is freely available again. To meet the needs of foundries requiring a bond with a rather greater moisture-holding capacity than Fulbond No. 1, Fulbond No. 3 has been developed, and this is also especially useful in foundries where the thorough milling which is desirable

<sup>1</sup> A Joint Committee of The Iron and Steel Institute and The British Iron and Steel Federation, reporting to The Iron and Steel Industrial Research Council.

<sup>2</sup> Included in the Third Report of the Steel Castings Research Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 23*, Section V., pp. 87–200.

to develop the full bonding power of Fulbond No. 1 is not possible. Foundry experience has shown that the ramming, casting and striping properties of the Fulbond mixtures are closely comparable to those of bentonite mixtures, and in reclamation plants the "life" of Fulbond is proving satisfactory. Fulbond can also be used satisfactorily as a suspensory agent in silica paint in place of bentonite.

A number of other substitutes for bentonite have been investigated in the laboratory and the foundry, but none of them appears to be so generally useful as a selected variety of Fulbond.

A considerable number of clay bonds have been investigated fully, and the trials show that some of them when used in proportions of 5-10% with a high-silica sand give satisfactory green strength but are lower in dry strength than normal Fulbond or bentonite mixtures. The clay-bonded sands have a greater hot strength than the Fulbond or bentonite mixtures, and in some branches of foundry work this is a definite advantage. Laboratory investigations and foundry trials indicate a useful field for mixtures of a good bond clay with Fulbond, the Fulbond addition improving the plasticity and dry strength without markedly reducing the hot strength. When mixtures of clay and Fulbond are used it is necessary that the mixing shall be thorough. Where stocks of bentonite have been in existence attention has been directed to means of conserving them by the use of Fulbond-bentonite and bentonite-clay mixtures.

An investigation on the production of steel moulding sands by the thorough grinding and admixture of selected clays with selected sandstones is in progress. Some of the sandstones examined contain from 7 to 12% of partially weathered feldspathic matter, and these have been shown to be a useful base for steel moulding sands; with the incorporation of 10-20% of clay the product has good general properties and can be diluted with silica sands to provide a range of strength and permeability. Special attention is being given to the weathered sandstones, such as those of the Wolsingham district of County Durham, which, because of their high content of "clay" from the decomposition of included feldspathic minerals, give, when thoroughly broken down by wet-grinding, a moulding sand which is satisfactory in general steel foundry use.

Experiments have been made with the addition of wetting agents to the water used in preparing moulding sands, but these additions do not appear to increase the rate of spread of the bond clay and have little effect on the strength of the moulding sand.

Investigations into the use of core binders have been made with particular reference to the possibility of effecting a reduction in the consumption of linseed oil and corn-starch products. It has been shown, for example, that in many cases up to one-half of the linseed oil in a core mixture can be replaced by Truline binder (a synthetic resinous material) without detriment to the strength and collapsability of the core. Truline binder is particularly effective where reclaimed

sands are used for core-making. Economies in the consumption of dextrin and other corn-starch products are of special importance, and attention is directed to the investigations which indicate the possibility of reducing the proportion of these materials in core mixtures by incorporating in the mixture a proportion of silica flour or a finely divided highly siliceous clay. One disadvantage of such mixtures is a reduction in permeability, but the trials which have been made indicate the possibility that undue importance has been attached to high permeability in cores. It has been shown in many instances that a reduction in the total quantity of core binders in a core sand does not result in any falling-off in performance.

As the quantity of sulphite lye available for use in foundries is decreasing, investigations have been made of possible alternatives which would have a similar behaviour in core mixtures. The use of "clay" binders in core mixtures has been examined, and the indications are that the incorporation of a proportion of a naturally bonded sand, a synthetic clay-bonded sand, bentonite, Fulbond or bond clay gives satisfactory results and renders possible an effective reduction in the proportion of organic binders. It must be borne in mind that highly colloidal bond clays, such as bentonite and Fulbond, tend to absorb an undue proportion of the organic bond, and that the proportion of clay bond must be limited so as to avoid poor collapsibility of the cores after casting.

Owing to the necessity for increasing the production of silica sands and fine core sands, and to reduce the long-distance transport of sands, a large number of additional sources have been investigated fully. A number of these are now in use in foundries in the various steelmaking areas. These investigations are to be reported fully in a separate paper, but it is gratifying to note here that imported sands have, in the main, been satisfactorily replaced by home resources.

To provide information needed by the Foundry Practice Subcommittee, investigations of the thermal expansion of sand mixtures containing clay, and of mixtures of low thermal conductivity suitable for use in certain types of feeder head, have been made.

Special attention is directed to the desirability of the calibration of pressure gauges on hydraulic machines for the measurement of dry strength. In other work on the testing of sands a new simple type of permeability apparatus has been developed, which gives accurate results for sands of both high and low permeability; a full account of this apparatus is given.

An investigation on the hot strength of moulding sands is in progress, and it seems likely that its results will provide data of definite value to foundries, especially when considered in conjunction with high-temperature sintering tests. Methods for measuring the plasticity of moulding and core sands and the surface characteristics of sands are also the subject of investigation.

The Sub-Committee have been able to render service to numerous steel foundries where troubles have arisen in the supply or use of moulding or core sands and they have collaborated with the British Cast Iron Research Association and the British Non-Ferrous Metals Research Association in matters of mutual interest. Much work has been done on behalf of the Foundry Bonding Materials Control of the Ministry of Supply.

*Constitution of the Moulding Materials Sub-Committee.*

Since the First Report was published, certain changes in the personnel of the Sub-Committee have occurred, and the constitution now is as follows :

*Dr. W. J. REES, <i>Chairman</i>	Sheffield University (also representing the British Cast Iron Research Association).
*Mr. T. R. WALKER, <i>Secretary</i>	English Steel Corporation, Ltd. (also representing the Institute of British Foundrymen).
Dr. C. H. DESCH, F.R.S.	The Iron and Steel Industrial Research Council.
Mr. G. T. HAMPTON	Messrs. F. H. Lloyd & Co., Ltd.
Mr. J. E. MERCER	Messrs. Head, Wrightson & Co., Ltd. (also representing the General Steel Castings Association).
*Mr. D. A. OLIVER	Messrs. Wm. Jessop & Sons, Ltd.
*Dr. R. J. SARJANT	Messrs. Hadfields, Ltd.
Mr. J. J. SHEEHAN	Coneygre Foundry, Ltd.
Mr. A. WHEELER	Messrs. Edgar Allen & Co., Ltd.

Those Members against whose names an asterisk is placed are Members of the Technical Advisory Committee of the Foundry Bonding Materials Control.

Mr. R. H. S. Robertson, of the Fullers' Earth Union, Ltd., Mr. W. B. Parkes, of the British Cast Iron Research Association, and Mr. J. Lumsden, of the Foundry Bonding Materials Control, have attended numerous meetings of the Sub-Committee by invitation, for purposes of liaison.

## SECTION II.—MOULDING SANDS.

### PART I.—*Examination of Moulding Sands.*

One of the objects of the Sub-Committee from its inception was to continue Boswell's examination of possible British alternatives to Belgian and French moulding sands. A number of moulding sands of domestic origin were investigated before the war began, and the results were published in the First Report of the Sub-Committee.<sup>1</sup> Since then the work has been carried on continuously.

<sup>1</sup> Third Report of the Steel Castings Research Committee, Section V., p. 87, *Iron and Steel Institute*, 1938, *Special Report No. 23*.



Several additional deposits have been developed; others have been surveyed and representative samples of sand obtained from them. Observations on the deposits and the results of testing sand samples are given below.

*Moulding Sand from the Raynham Estate, Fakenham, Norfolk.*

The deposit of this sand is said to be of considerable extent, and the sample examined was representative of the bulk which could be supplied for use. The sample as received contained a large number of agglomerated lumps; these were all crushed and the whole of the bulk sample was then thoroughly mixed before quartering to obtain the sample for the tests.

*Chemical Analysis.*

Chemical analysis on a sample dried at 105° C. gave the following results :

Silica . . . . .	85.65%
Alumina . . . . .	6.04%
Iron oxide . . . . .	3.28%
Titanium oxide . . . . .	0.38%
Lime . . . . .	0.95%
Magnesia . . . . .	0.14%
Alkalis (as K <sub>2</sub> O) . . . . .	0.82%
Loss on ignition . . . . .	2.65%
	<hr/>
	99.91%

*Refractoriness.*

By comparison with standard cones, the refractoriness was equivalent to that of cone 27 (1610° C.).

*Mechanical Analysis.*

The following is the sieve analysis of the material :

B.S.I. Sieves.	
On 10 mesh . . . . .	Nil
„ 16 „ . . . . .	0.2%
„ 22 „ . . . . .	0.4%
„ 30 „ . . . . .	0.4%
„ 44 „ . . . . .	1.3%
„ 60 „ . . . . .	4.4%
„ 72 „ . . . . .	6.7%
„ 100 „ . . . . .	19.0%
Thro' 100 „ . . . . .	67.6%
	<hr/>
	100.0%

*Compression Strength.*

The compression strength of green-sand test-pieces was found to be as follows :

Water added to dry sand.									
% . . . . .	1	2	3	4	5	6	7	8	9
Compression, green strength.									
Lb. per sq. in. . . . .	0	2.2	5.4	7.3	9.2	7.3	6.7	6.5	6.0

The optimum green strength was obtained, as shown above, with a moisture content of 5%.

### *Dry Compression Strength.*

The compression strength of test-pieces made with a 5% moisture content, dried at 200° C., was 105 lb. per sq. in.

### *Permeability.*

The permeability number of green-sand test-pieces with a 5% moisture content for optimum green strength was 18.

As shown by the mechanical analysis, this sand is of fine grain size, and in consequence its permeability is rather low. It would probably be satisfactory for use in iron foundries, but actual foundry trials would be necessary to determine its suitability for general purposes.

### *Bonding Properties.*

The refractoriness and strength of the sand are high enough to permit of its use in steel casting, but the permeability is too low. Tests were therefore made of mixtures of the sand with Arnold's Leighton Buzzard No. 52 sand, which is a moderately coarse-grained high-silica sand, with the following results :

#### *Equal Weights of Raynham Sand and Arnold's No. 52 Sand.*

Optimum green strength with 4.5% of moisture .	5.4 lb. per sq. in.
Permeability No. . . . .	40
Dry strength . . . . .	55 lb. per sq. in.

#### *Two Parts by Weight of Raynham Sand to Three Parts of Arnold's No. 52 Sand.*

Optimum green strength with 4.5% of moisture .	4.4 lb. per sq. in.
Permeability No. . . . .	52
Dry strength . . . . .	40 lb. per sq. in.

#### *One Part by Weight of Raynham Sand to Two Parts of Arnold's No. 52 Sand.*

Optimum green strength with 4.0% of moisture .	3.0 lb. per sq. in.
Permeability No. . . . .	70
Dry strength . . . . .	22 lb. per sq. in.

It is apparent from these last three tests that there is a definite possibility of utilising this sand in steel foundries by diluting it with from 1 to 1½ times its weight of a high-silica sand, such as Arnold's No. 52 sand.

### *Park Moulding Sand, from Redhill, Surrey.*

This sand occurs above the fullers' earth beds at Redhill, and is supplied by the Fullers' Earth Union, Ltd., as a friable sandstone which breaks down easily on milling. The quartz grains are sub-angular to rounded in form and are well coated with limonite. Abundant small grains of glauconite give a greenish tint to the sand. These glauconite grains add considerably to the bond strength of

sand, for, on milling, they crumble to a fine powder which adheres to the quartz grains.

Although the raw sand is of comparatively low refractoriness, the mixtures with 1-2 parts of silica sand appear to be refractory enough for steel-foundry use. As will be seen from the bonding properties tabulated below, such mixtures are quite strong enough for normal foundry work.

### Mechanical Analysis.

The following is the sieve analysis of this sand :

B.S.I. Sieves.				
On	5 mesh	.	.	0.3%
"	8 "	.	.	0.3%
"	10 "	.	.	0.4%
"	16 "	.	.	2.3%
"	22 "	.	.	2.9%
"	30 "	.	.	5.8%
"	44 "	.	.	14.6%
"	60 "	.	.	26.6%
"	72 "	.	.	7.9%
"	100 "	.	.	15.1%
"	150 "	.	.	10.2%
Thro'	150 "	.	.	13.6%
				<hr/> 100.0%

### Refractoriness.

Test-pieces were fired at 1550° C. for 2 hr., with the following results :

*Park Sand Alone.*—Test-pieces fused completely.

*One Part of Park Sand to one Part of Arnold's 52 Sand.*—Test-pieces dark brown; grains well fritted together. Test-pieces expanded 2.5% both laterally and longitudinally.

*One Part of Park Sand to Two Parts of Arnold's 52 Sand.*—Test-pieces dark brown; grains fritted. Test-pieces expanded 10% both laterally and longitudinally.

### Bonding Properties.

All test-pieces were of A.F.A. dimensions, and were rammed with 10 blows. The results of permeability and green and dry strength tests are recorded below :

#### *Park Sand Alone.*

Bulk density	.	.	.	1.8	1.82	1.85	1.9
Moisture content.	%	.	.	7.9	8.7	9.6	11.0
Permeability No.	.	.	.	17	14	13	5
Green strength.	Lb. per sq. in.	.	.	31.2	34.2	38.0	31.9
Dry strength.	Lb. per sq. in.	.	.	197	219	260	334

#### *One Part of Park Sand to One Part of Arnold's 52 Sand.*

Bulk density	.	.	.	1.77	1.81	1.85	1.93
Moisture content.	%	.	.	4.6	5.3	6.4	8.0
Permeability No.	.	.	.	111	88	75	70
Green strength.	Lb. per sq. in.	.	.	24.5	22.3	19.7	13.9
Dry strength.	Lb. per sq. in.	.	.	95	112	124	164

*One Part of Park Sand to Two Parts of Arnold's 52 Sand.*

Bulk density	. . . .	1.65	1.67	1.72	1.74
Moisture content.	% . . . .	2.7	3.9	4.7	6.8
Permeability No.	. . . .	168	156	140	105
Green strength.	Lb. per sq. in.	10.8	10.7	8.3	6.0
Dry strength.	Lb. per sq. in.	19.7	28.6	50.0	73.5

*One Part of Park Sand to Two Parts of Chelford Sand.*

Bulk density	. . . .	1.65	1.70
Moisture content.	% . . . .	3.2	4.6
Permeability No.	. . . .	96	81
Green strength.	Lb. per sq. in.	11.7	11.4
Dry strength.	Lb. per sq. in.	23	48

*Moulding Sand from a Quarry near Melksham, Wiltshire.*

This naturally bonded red sand is being worked by Messrs. Simmonds & Sons, Frenchay, Bristol. It is being used in a Bristol steel foundry, and the sample was obtained from that foundry.

*Mechanical Analysis.*

The following is the sieve analysis of this material :

B.S.I. Sieves.				
On 10 mesh	. . . .	Nil		
" 16 "	. . . .	1.6%		
" 22 "	. . . .	1.9%		
" 30 "	. . . .	7.7%		
" 44 "	. . . .	29.0%		
" 60 "	. . . .	40.3%		
" 72 "	. . . .	9.4%		
" 100 "	. . . .	8.4%		
" 150 "	. . . .	1.1%		
Thro' 150 "	. . . .	0.6%		
		<hr/> 100.0% <hr/>		

"Clay" content by elutriation, 8.5-9.0%.

*Strength and Permeability.*

Test cylinders, 2 in.  $\times$  2 in., were rammed in an A.F.A. apparatus, the number of blows being 10. The following are the test results obtained :

Bulk density	. . . .	1.65	1.68	1.68	1.71
Moisture content.	% . . . .	3.2	4.1	4.7	5.0
Permeability No.	. . . .	183	175	150	190
Green strength.	Lb. per sq. in.	6.3	3.4	3.3	3.1
Dry strength.	Lb. per sq. in.	35.6	64.9	71.3	71.6

*Refractoriness.*

Test-pieces fired for 2 hr. at 1550° C. were dark brown in colour and showed an expansion of 5%. Slight fritting or sintering was apparent, but there was no actual fusion or distortion.

# *Practical Use of the Sand.*

The following information was supplied by the foundry using the sand : “ We are using this sand for light steel castings in green sand. For small castings in dry-sand work we make an addition of 5% of air-floated Devon ball-clay, which is somewhat stronger in bonding properties than the proprietary clays such as Colbond. For moulding dry-sand work, we make an addition of 25% of Leighton Buzzard silica sand, and 8% of air-floated ball clay. The consistency of the sand as received from the pit is fairly constant. This is a new deposit, and the latest samples tend to show a higher clay content, but the grain size remains constant.”

## *I.M. Sand and “ Serumite ” Bonding Clay from Western Foundry Supplies, Ltd., Bournemouth.*

The I.M. sand is the sand occurring at the top of the measures in the quarry between Bournemouth and Poole, and is the base sand, used with the clay occurring immediately below the sand, in the production of the Dorset moulding sand.

The “ Serumite ” bonding clay is the above clay dried and finely ground. It is available as a commercial product, and can thus be used for bonding sands other than the I.M. sand with which it occurs naturally.

## *Mechanical Analysis.*

The following is the sieve analysis of I.M. sand :

B.S.I. Sieves.				
On 10 mesh	.	.	.	Nil
“ 16 ”	.	.	.	0.1%
“ 22 ”	.	.	.	0.5%
“ 30 ”	.	.	.	3.0%
“ 44 ”	.	.	.	18.0%
“ 60 ”	.	.	.	46.8%
“ 72 ”	.	.	.	12.0%
“ 100 ”	.	.	.	15.8%
“ 150 ”	.	.	.	2.6%
Thro’ 150 ”	.	.	.	1.2%
				<hr/> 100.0% <hr/>

## *Permeability and Strength.*

The permeability and strength of I.M. sand alone and bonded with Serumite and of the latter bonded with Arnold’s No. 52 sand and Chelford sand are stated below :

<i>I.M. Sand Alone.</i>				
Bulk density .	.	.	.	1.65
Moisture content. %	.	.	.	2.0
Permeability No.	.	.	.	300
Green strength. Lb. per sq. in.	.	.	.	3.7
Dry strength. Lb. per sq. in.	.	.	.	1.6
1942—ii				
				1.65
				2.5
				350
				2.8
				4.3
				D D



*I.M. Sand Bonded with Serumite Clay.*

Serumite. %	5	5	10	15	15	20	20	20
Bulk density	1.66	1.67	1.70	1.77	1.80	1.80	1.85	1.90
Moisture content.								
%	2.8	3.2	5.2	6.1	8.2	7.1	8.2	9.0
Permeability No.	300	300	191	124	124	70	68	32
Green strength.								
Lb. per sq. in.	10.7	10.1	21.0	25.2	18.8	27.9	21.3	22.0
Dry strength.								
Lb. per sq. in.	8.0	9.1	66	106	114	96	116	151

*Arnold's No. 52 Sand Bonded with Serumite Clay.*

Serumite. %				7.5	7.5	10.0	10.0
Bulk density				1.61	1.63	1.65	1.67
Moisture content. %				1.4	1.9	2.0	2.5
Permeability No.				350	300	260	235
Green strength. Lb. per sq. in.				4.5	3.8	8.6	6.5
Dry strength. Lb. per sq. in.				3.8	6.5	6.7	12.1

*Chelford Sand Bonded with Serumite Clay.*

Serumite. %				7.5	7.5	10.0	10.0
Bulk density				1.65	1.67	1.69	1.71
Moisture content. %				2.0	2.6	2.1	2.5
Permeability No.				110	91	86	84
Green strength. Lb. per sq. in.				7.0	6.7	9.2	10.8
Dry strength. Lb. per sq. in.				4.6	12.5	11.1	18.1
							25.8

*Refractoriness.*

A.F.A. test-pieces were heated at 1550° C. for 2 hr., with the following results :

*I.M. Sand.*—Grains fritted, but no actual fusion. No volume change.

*I.M. Sand with Serumite.*—With 5% of Serumite there is more fritting than with the raw sand alone and a shrinkage of 2½%. The fritting and shrinkage increase with an increase in the proportion of Serumite; with 20% of Serumite the surfaces of the test-pieces show slight glazing and a shrinkage of 5%.

*Arnold's No. 52 Sand and Chelford Sand with Serumite.*—These test-pieces show slight fritting, increasing with the proportion of bond, but less than with the corresponding mixtures based on I.M. sand.

*General Remarks.*

All the above mixtures are sufficiently refractory for steel-foundry use. These tests emphasise the usefulness of a sand which naturally has a ferruginous coating on the sand grains as the basis for a synthetic moulding sand. The Serumite bonding clay has no outstanding properties, but is a useful bond clay, and "fits" especially well with the ferruginous I.M. sand.

*Sand from Brookside Farm, Higher Kinnerton, near Chester.*

The results of tests made on a sample bag of sand from the above deposit, from which, it is believed, a considerable tonnage of sand similar to this sample could be obtained, are given below. The sand is red in colour and has a natural bond.

*Chemical Analysis.*

The following is the chemical analysis of the dried sample :

Silica . . . . .	92.15%
Alumina . . . . .	2.12%
Iron oxide . . . . .	1.65%
Titanium oxide . . . . .	0.18%
Lime . . . . .	0.25%
Magnesia . . . . .	0.42%
Alkalis (as $K_2O$ ) . . . . .	1.83%
Loss on ignition . . . . .	1.40%
	<hr/>
	100.00%
	<hr/>

*Mechanical Analysis.*

Sieve analysis gave the undermentioned results :

B.S.I. Sieves.	
On 10 mesh . . . . .	Nil
„ 16 „ . . . . .	0.1%
„ 22 „ . . . . .	0.1%
„ 30 „ . . . . .	0.2%
„ 44 „ . . . . .	0.3%
„ 60 „ . . . . .	10.6%
„ 72 „ . . . . .	11.5%
„ 100 „ . . . . .	40.7%
„ 150 „ . . . . .	28.4%
Thro' 150 „ . . . . .	8.1%
	<hr/>
	100.1%
	<hr/>

“ Clay ” content by elutriation, 8.0–9.0%.

*Strength and Permeability Tests.*

A.F.A. test-pieces were rammed with 10 blows, and gave the following results on test :

Bulk density . . . . .	1.63
Permeability No. . . . .	53
Green strength . . . . .	6.2 lb. per sq. in.
Dry strength . . . . .	39.1 lb. per sq. in.

*Refractoriness.*

Test-pieces fired for 2 hr. at  $1550^{\circ}$  C. showed a shrinkage of 10% with a slightly glazed surface but no squatting or pronounced fusion. The original red-brown colour changed to a grey colour. This is probably due to reaction between the iron oxide and magnesia shown in the chemical analysis.

*General Remarks.*

This sand has useful properties and merits further investigation. It is possible that it could be used in steel foundries as well as in iron and non-ferrous foundries, but a foundry trial would be necessary before forming a definite opinion as to its value for steel casting.

*Three Sandstones from the Durham Area.*

These are naturally bonded sandstones, marketed by the Northern Sand Supply Company, and were received in the partly crushed state from a steel foundry in which they are used. They are typical rotten rocks having a sericitic bond.

*Mechanical Analysis.*

The following are the sieve analyses of the three sandstones :

B.S.I. Sieves.	Eastgate Fine.	Eastgate Rock Sand.	Northern Cleugh Sand.
On 5 mesh	Nil	0.1%	0.2%
" 8 "	0.3%	1.6%	1.6%
" 10 "	0.2%	1.1%	1.4%
" 16 "	4.8%	24.2%	21.5%
" 22 "	3.8%	17.3%	16.2%
" 30 "	5.6%	18.4%	17.8%
" 44 "	8.4%	14.4%	13.8%
" 60 "	18.4%	10.4%	11.2%
" 72 "	9.0%	2.3%	2.5%
" 100 "	28.8%	4.4%	6.6%
" 150 "	12.8%	2.6%	3.6%
Thro' 150 "	7.8%	3.0%	3.5%
	99.9%	99.8%	99.9%

*Refractoriness.*

Test-pieces were fired for 2 hr. at 1520° C., with the following results :

*Eastgate Fine.*—Test-piece brown and glazed. Shrinkage, 10% on both the length and the diameter.

*Eastgate Rock Sand.*—Test-piece mottled, grains fritted. Shrinkage, 2.5% on both the length and the diameter

*Northern Cleugh Sand.*—Test-piece mottled, grains fritted. Expansion, 2.5% on both the length and the diameter.

*Moulding Properties.*

A.F.A. test cylinders, 2 in. × 2 in., were rammed with 10 blows; the test results were as follows :

	Eastgate Fine.	Eastgate Rock Sand.	Northern Cleugh Sand.
Bulk density	1.75	1.92	1.92
Moisture content. %	7.8	7.0	7.2
Permeability No.	214	256	236
Max. green strength. Lb. per sq. in.	26.8	29.2	23.5
Dry strength. Lb. per sq. in.	114	234	199

*Sand from Dead Friars Quarries.*

This sand occurs in the Dead Friars Quarries, Blanchland, County Durham. Two samples were taken at the quarry face, and another sample was collected from a wagon of sand delivered to the user.

# Mechanical Analysis.

Sieve analyses of the three samples gave the following results :

				Collected at Quarry.		
B.S.I. Sieves.						
On	8 mesh	.	.	From Wagon.	Main Face.	Right Face.
"	10	"	.	Nil	0.2%	0.1%
"	16	"	.	Nil	0.6%	0.2%
"	22	"	.	0.2%	6.6%	21.7%
"	30	"	.	13.5%	7.4%	15.9%
"	44	"	.	18.5%	14.4%	17.4%
"	60	"	.	20.4%	21.9%	16.4%
"	72	"	.	21.4%	21.3%	14.3%
"	100	"	.	4.1%	4.9%	2.8%
"	150	"	.	8.1%	9.4%	4.4%
Thro'	150	"	.	5.1%	5.6%	2.6%
				8.7%	7.7%	4.2%
				100.0%	100.0%	100.0%

# Bond Strength and Permeability Tests.

The results of tests on the bond strength and permeability follow :

Sample from Wagon.					
Moisture.	%	.	.	3.6	4.1
Permeability No.	.	.	.	42	58
Green strength.	Lb. per sq.			5.0	6.0
in.	.	.	.	60	60
Dry strength.	Lb. per sq. in.			18.1	18.2
				20.4	25.5
				25.8	22.0
				150.2	180.7
				182.3	

# Samples Collected from Quarry.

		Main Face.		Right Face.	
Moisture.	% . . . . .	6.7	8.6	6.2	7.7
Permeability No.	. . . . .	38	32	40	32
Green strength.	Lb. per sq.				
in.	. . . . .	21.3	19.7	21.0	13.4
Dry strength.	Lb. per sq. in.	179.0	189	142	144

# Sample from Wagon milled with Arnold's Leighton Buzzard No. 52 Sand.

				Two Parts of Blanchland to One Part of Silica Sand.			Equal Parts of Blanchland and Silica Sand.		
Moisture.	%	.	.	3.8	5.0	5.7	3.1	4.1	4.8
Permeability No.	.	.	.	71	96	88	95	98	91
Green strength.	Lb. per sq.								
in.	.	.	.	8.6	10.0	6.1	7.0	7.2	7.7
Dry strength.	Lb. per sq. in.			80.5	88.1	91.0	15.3	18.5	24.5

# Refractoriness.

Test-pieces from all the samples after firing for 3 hr. at 1550° C. showed fritting but no actual fusion. The material from the right face was more refractory, but rather weaker in bond, than the main face material or the "run-of-quarry" material supplied in the

wagon. The refractoriness is quite satisfactory for the material to be used in steel foundries.

### *General Remarks.*

The samples taken at the quarry are a little coarser in grain size than that from the wagon; probably the latter is likely to be more representative of the run-of-quarry material.

The tests made indicate that the run-of-quarry material is quite comparable in general properties and quality with that produced, and milled, at other quarries in the Tow-Law/Stanhope area.

The milled product from a heavy mill is stronger and better as a moulding sand than that from a light mill; heavy milling gives a better grading and better distribution of the bond.

### *Leighton Buzzard (Messrs. J. Arnold & Sons, Ltd.) Steel Moulding Sand No. 27.*

The following is the sieve analysis of the material :

B.S.I. Sieves.				
On	5 mesh	.	.	Nil
"	10	"	.	0.5%
"	16	"	.	0.2%
"	22	"	.	0.2%
"	30	"	.	0.4%
"	44	"	.	0.7%
"	60	"	.	1.6%
"	72	"	.	1.7%
"	100	"	.	12.5%
Thro'	100	"	.	82.2%

"Clay" grade by elutriation (included in "through 100 mesh"), 15.9%.

By comparison with standard cones the refractoriness was found to be 1670° C.

The following bond-strength and permeability values were obtained :

#### *Sand as received, dried at 110° C.*

Moisture.	%	.	.	3	5	7	15
Core weight.	G.	.	.	165	165	165	195
Green strength.	Lb. per sq. in.	.	.	17.9	18.5	17.3	8.9
Dry strength.	Lb. per sq. in.	.	.	...	71	86	388

Permeability No. at 5% moisture, 46.5.

Mixtures of this material with Arnold's 52 sand and with Chelford sand gave the following results :

#### *Two Parts of Arnold's 52 Sand to one of Special 27.*

Moisture.	%	.	.	1.5	2.0	3.0	6.0
Core weight.	G.	.	.	170	170	170	190
Green strength.	Lb. per sq. in.	.	.	5.15	5.89	4.93	2.47
Dry strength.	Lb. per sq. in.	.	.	...	...	...	116

Permeability No. at 2.0% moisture, 92.8.



*Two Parts of Chelford Sand to one of Special 27.*

Moisture. %	.	.	.	.	1.5	2.0	3.0	6.5
Core weight. G.	.	.	.	.	170	170	170	180
Green strength. Lb. per sq. in.	.	.	.	.	5.02	<b>5.81</b>	4.97	2.55
Dry strength. Lb. per sq. in.	.	.	.	.	...	...	...	141

Permeability No. at 2.0% moisture, 69.5.

*Three Parts of Arnold's 52 Sand to one of Special 27.*

Moisture. %	.	.	.	.	1.0	1.5	2.0	3.0
Core weight. G.	.	.	.	.	165	165	170	175
Green strength. Lb. per sq. in.	.	.	.	.	2.81	<b>4.00</b>	3.70	2.49
Dry strength. Lb. per sq. in.	.	.	.	.	...	...	...	35

Permeability No. at 1.5% moisture, 150.

*Three Parts of Chelford Sand to one of Special 27.*

Moisture. %	.	.	.	.	1.0	1.5	2.0	3.5
Core weight. G.	.	.	.	.	170	170	170	175
Green strength. Lb. per sq. in.	.	.	.	.	2.91	<b>3.89</b>	3.53	2.36
Dry strength. Lb. per sq. in.	.	.	.	.	...	...	...	40

Permeability No. at 1.5% moisture, 117.

Test-pieces of the above four mixtures sintered at 1600° C.

The better bond strength given by admixture with Arnold's 52 sand is probably due to the improved grading obtained. The grains would seem to pack in a manner conducive to greater strength.

*Moulding Sand from The Alderley Edge Red Moulding Sand Co., Ltd.,  
Alderley Edge, Cheshire.*

This deposit is of considerable extent, and the samples examined were the unmilled soft sandstone and the prepared milled moulding sand. The unmilled material is a soft crumbly sandstone composed of rounded quartz grains and aggregates, more or less coated with a ferruginous (limonitic) clay.

*Chemical Analysis.*

Chemical analysis on samples dried at 105° C. gave the following results :

	Unmilled.	Milled.
Silica . . . . .	86.58%	88.85%
Alumina . . . . .	7.45%	5.75%
Iron oxide . . . . .	0.96%	0.85%
Titanium oxide . . . . .	0.31%	0.25%
Lime . . . . .	0.48%	0.45%
Magnesia . . . . .	0.51%	0.40%
Alkalis (as K <sub>2</sub> O) . . . . .	1.96%	1.85%
Loss on ignition . . . . .	1.65%	1.45%
	<hr/> 99.90%	<hr/> 99.85%

*Mechanical Analysis.*

The following are the results of sieve analyses on the material :

B.S.I. Sieves.	Unmilled Sample Milled in Laboratory.	Milled Sample.
On 5 mesh	Nil	Nil
" 8 "	0.2%	0.8%
" 10 "	0.2%	0.8%
" 16 "	0.3%	2.0%
" 22 "	0.3%	0.8%
" 30 "	1.0%	1.2%
" 44 "	7.9%	6.7%
" 60 "	23.2%	12.8%
" 72 "	9.6%	5.3%
" 100 "	24.9%	17.2%
" 150 "	18.0%	22.3%
Thro' 150 "	14.4%	30.1%
	100.0%	100.0%

The unmilled sample contained rather more clay than the sample supplied milled. It is probable that the latter had been ground in a mill much heavier than the laboratory mill and more of the quartzitic aggregates had been broken down. The milling tests indicate that fairly heavy milling is desirable to develop properly the bond strength of the sand.

*Moulding Properties.*

For these tests the sample supplied unmilled was milled in the laboratory; the test-pieces were rammed in the A.F.A. rammer, some with 3 blows, some with 10. The test results obtained were as follows :

	Unmilled Sample Milled in Laboratory. <i>Test-Pieces rammed 3 times.</i>				Milled Sample.			
Bulk density	1.61	1.61	1.62	1.60	1.60	1.60	1.60	1.62
Moisture. %	2.6	3.9	5.9	2.8	4.2	4.6	5.9	6.5
Permeability No.	71	63	52	120	106	106	88	82
Green strength. Lb. per sq. in.	7.4	6.0	4.0	4.7	3.5	3.1	2.7	2.5
Dry strength. Lb. per sq. in.	16.0	22.0	48.0	7.0	11.8	12.5	38.0	32.5
	<i>Test-Pieces rammed 10 times.</i>							
Bulk density	1.63	1.63	1.65	1.62	1.62	1.62	1.63	1.64
Moisture. %	2.6	3.9	5.9	2.8	4.2	4.6	5.9	6.5
Permeability No.	49	46	42	90	80	78	65	65
Green strength. Lb. per sq. in.	11.9	9.5	7.5	6.4	5.6	5.3	4.6	4.1
Dry strength. Lb. per sq. in.	23.0	32.0	72.0	12.0	22.6	28.0	57.0	53.5

*Refractoriness.*

The fusion point of the sample supplied unmilled was 1630° C. and of the milled sample 1650° C. Test-pieces fired at 1550° C. were grey-white in colour, the original red colour having changed owing to reactions between the iron oxide, lime, magnesia and silica.

This sand is refractory enough for steel-foundry use, but its bond strength would not allow of much dilution with a silica sand.

# PART 2.—*The Effect of Milling on the Properties of Moulding Sand.*

(Figs. 3 to 5 = Plate XXXVIII.)

The experiments recorded below show the effect of milling on the properties of moulding sand.

## *The Mixes Tested.*

Three green-sand mixes were prepared in a pan-mill at a steel foundry; the following are the details :

Diameter of pan	6 ft. 6 in.	Rotation of pan	30 r.p.m.
Diameter of rollers	1 ft. 10 in.	Mean surface velo-	450 ft. per min.,
Width of rollers	1 ft. 4 in.	city of pan	approx.
Weight of mix, 5 cwt.			

The composition of the mixes was the same as that used for ordinary green-sand work in the foundry, viz. :

South Cave Sand.	Chelford Sand.	Bentonite.	Water.
25%	75%	3%	3-4%

The South Cave sand was moist when used, while the Chelford sand was air-dry. Extra water was added to increase the moisture content to 3-4%.

The first two mixes were prepared according to the usual practice at the foundry, and the samples were removed from the mill at intervals, the final sample being taken after 4 min. milling. The third mix was prepared by an exceptionally long milling, the final sample being taken after 20 min. milling.

## *Green Strength.*

The first mix was tested in the foundry laboratory, while the second and third mixes were tested in the Refractories Department of Sheffield University.

TABLE I.—*Tests in Foundry Laboratory.*

Milling Time. Min. : Moisture Content. % :	½. 2·5.	1. 3·25.	2. 3·25.	3. 3·5.	4. 3·5.
No. of Rams.	<i>A.—Green Strength. Lb. per sq. in.</i>				
3	4·9	5·7	6·5	6·8	6·5
9	7·2	8·3	13·1	12·7	13·1
15	8·7	9·7	14·3	14·3	15·3
20	...	10·8	15·9	16·2	15·9
40	...	15·3	19·1	17·5	18·9
	<i>B.—Permeability Number.</i>				
3	146	169	209	209	209
9	101	111	135	133	135
15	85	96	111	111	111
20	...	82	103	103	103
40	...	72	77	77	77

Test-pieces of A.F.A. dimensions were used in these tests. In the foundry laboratory (*see* Table I.) strengths less than 9 lb. per sq. in. were determined in a B.C.I.R.A. machine using a spring balance, while strengths more than 9 lb. per sq. in. were determined in a lever machine using lead-shot loading. In the Refractories Department (*see* Table II.) the green strengths were determined in a

TABLE II.—*Tests in Refractories Department, Sheffield University.*

Milling Time. Min.: Moisture Content. %:	$\frac{1}{2}$ . 2.5.	1. 3.25.	2. 3.25.	3. 3.5.	4. 3.5.
No. of Rams.	<i>A.—Green Strength. Lb. per sq. in.</i>				
3	3.3	5.4	6.4	6.7	7.2
9	6.5	7.1	10.5	9.9	10.6
15	6.5	9.3	12.2	11.5	13.1
20	6.6	10.2	12.4	13.0	15.3
30	...	...	14.5	15.5	17.5
40	8.9	10.7	16.1	17.4	17.2
	<i>B.—Permeability Number.</i>				
3	171	177	192	185	192
9	138	147	148	148	148
15	120	129	129	134	127
20	118	116	116	122	116
30	...	...	107	107	110
40	100	97	91	91	96

B.C.I.R.A. machine, of which the maximum reading was equivalent to 18 lb. per sq. in. The determination of the green strength raises the problem of the ramming of the test-pieces. In the standard A.F.A. test, the test-pieces are compacted by 3 blows of the rammer. The sand in such test-pieces is not so compact as the sand after ramming in ordinary foundry practice.

It will be seen from Fig. 1<sup>1</sup> that the green strength of test-pieces prepared by 3 blows of the rammer is not directly related to that of test-pieces prepared by 20 or 40 blows. With the exception of the curve for 3 blows, the curves show that the green strength increases rapidly in the first 2 min. milling and thereafter continues to increase slowly. The curve for 3 blows suggests that the green strength does not increase rapidly after the first minute of milling.

In Fig. 2<sup>1</sup> the green strength is plotted against the number of blows of the rammer in order to show that, for the mix employed, the green strength after 15–20 blows is increased but slightly by further ramming. The proximity to each other of the curves for 2, 3 and 4 min. milling emphasises that the green strength scarcely increases after 2 min. milling, and their distance from the  $\frac{1}{2}$ - and 1-min. curves stresses the rapid increase in green strength in the early stages of milling.

<sup>1</sup> Graphs based on the tests made on the second mix—*see* Table II.

The mix prepared by extra long milling was no stronger than that prepared by ordinary milling.

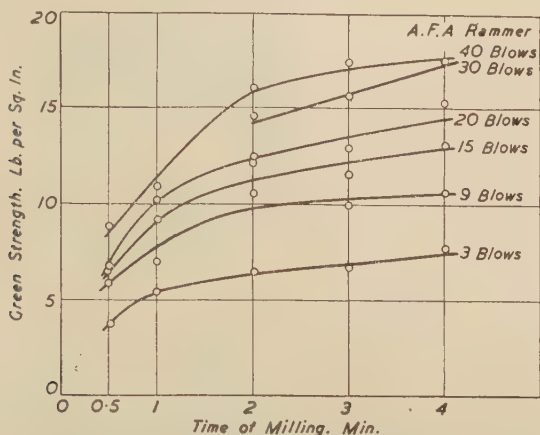


FIG. 1.—Relation between Green Strength and Time of Milling for Different Numbers of Rammer Blows.

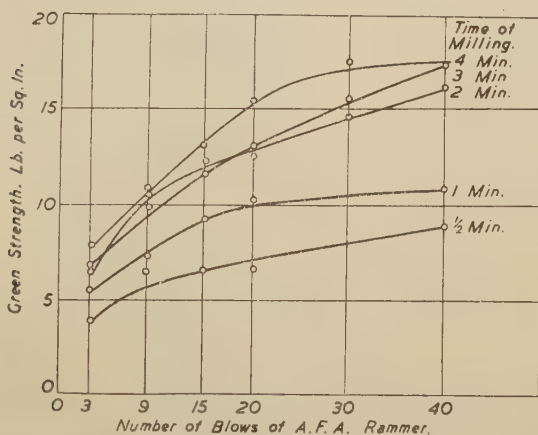


FIG. 2.—Relation between Green Strength and Number of Rammer Blows for Different Milling Times.

### Dry Strength.

Standard A.F.A. test-pieces (3 rams) of the green-sand samples were dried at 200° C. for 2 hr. The test-pieces were then removed from the oven and allowed to cool to room temperature for 2 hr. Compression tests were made in a Ridsdale compression machine in the Refractories Department. The results are given in Table III. ;



TABLE III.—*Dry Strength.*  
Strength expressed in lb. per sq. in.

Milling Time.				
$\frac{1}{2}$ min.	1 min.	2 min.	3 min.	4 min.
24	54	66	72	62 ?
22	49	72	66 ?	65
22	50	67	69	68
23	48	70	72	66
22.75 av'ge	50.25 av'ge	68.75 av'ge	69.75 av'ge	65.25 av'ge

the dry strength increases more rapidly during the first 2 min. milling.

### *Grading.*

Sieving tests showed that :

(1) The grading of the sample taken after  $\frac{1}{2}$  min. milling varied beyond the limits of experimental error—that is, the Chelford and South Cave sands were incompletely mixed.

(2) The grading of the sample taken after 4 min. milling was almost the same as the average for the  $\frac{1}{2}$ -min. sample—that is, milling for 4 min. does not reduce the grain size appreciably. Aggregates of quartz grains bonded with limonite, up to 0.5 in. across, were as numerous in the 4-min. sample as in the  $\frac{1}{2}$ -min. sample.

### *Permeability.*

The permeability number (after 3 blows of the rammer) of the samples taken after two or more minutes' milling was 190, compared with 170 for the  $\frac{1}{2}$ -min. sample. This is to be expected from the micro-examination (*see below*), for after 2 min. milling the bond is fairly well distributed over the grains. Consequently the diameter of most grains is slightly increased and the porosity is correspondingly increased. Furthermore, milling distributes the moisture evenly, so that the bond swells uniformly.

The permeability number after 40 blows of the rammer is 90–100, irrespective of the amount of milling. It depends on the grading of the quartz grains only, for the sand is so tightly packed that the grains are not separated by bond.

### *Micro-Examination.*

Examination of the samples shows that milling distributes the bond more evenly over the grains. South Cave sand is heavily coated with limonite (*see Fig. 3*). The effect of milling on the distribution of the bond may be summarised as follows :

$\frac{1}{2}$  min. Milling.—Chelford and South Cave sands are easily distinguished.

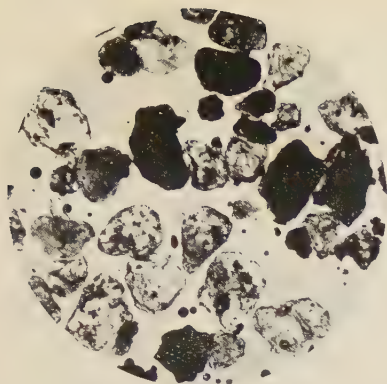


FIG. 3.—Half-Minute Milling. South Cave grains opaque; Chelford grains transparent.

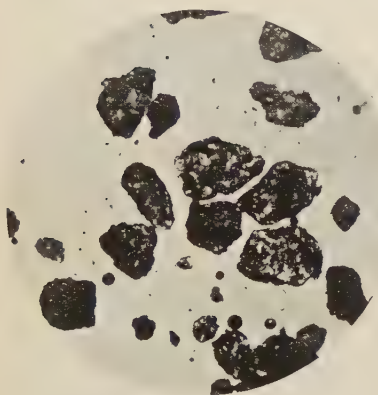


FIG. 4.—Two-Minute Milling. South Cave grains still opaque; Chelford grains partly transparent.



FIG. 5.—Four-Minute Milling. South Cave and Chelford grains equally coated with bond, thus being indistinguishable.

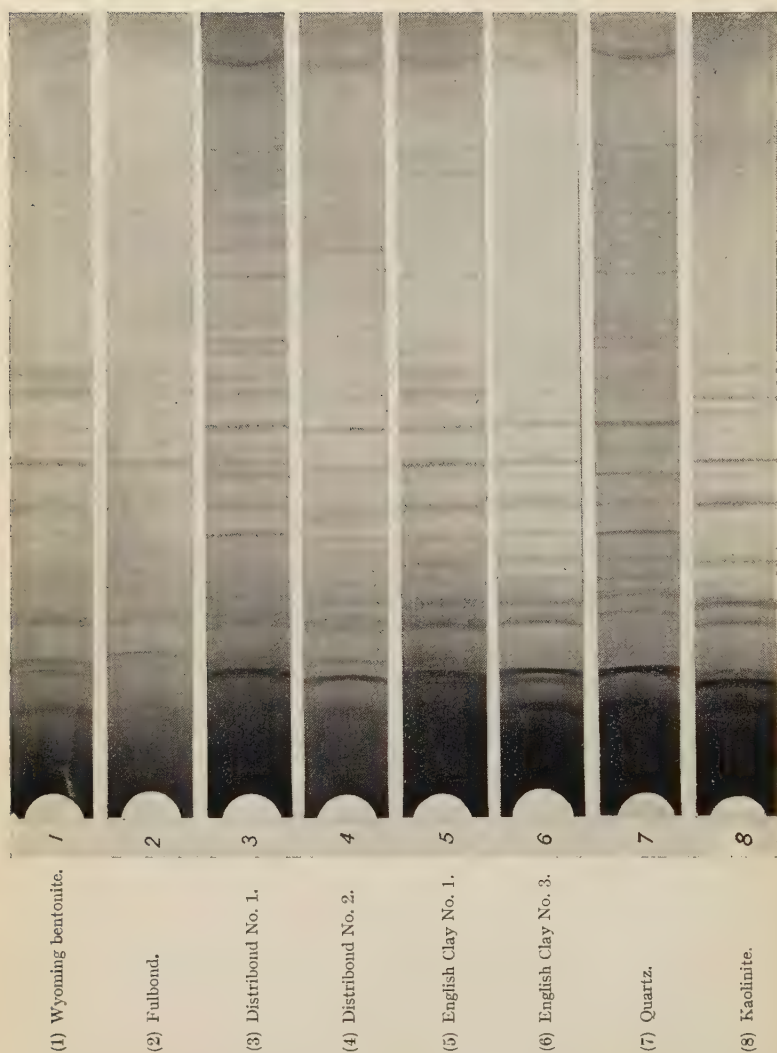


FIG. 12.—X-Ray Powder Photographs.

[Second Report of the Moulding Materials Sub-Committee.

[Section III., Part 2.

[To face p. 413 p.

1 min. *Milling*.—Chelford sand becomes browner, owing to the adhesion of limonite derived from the South Cave sand. The two sands are still easily distinguished.

2 min. *Milling*.—South Cave sand can still be distinguished by its heavy coat of limonite. The Chelford grains become browner, owing to the adhesion of still more limonite (see Fig. 4).

3 min. *Milling*.—The distribution of the limonite through the mixture is nearly uniform, and heavily coated grains are few.

4 min. *Milling*.—The limonite bond is uniformly distributed over all the sand grains, heavily coated grains being rare (see Fig. 5).

Both the South Cave and Chelford sand grains are subangular. Consequently milling has little effect on the grain shape, except for a few grains which have broken into angular fragments.

It is thus possible, by micro-examination, to tell whether a green-sand mix has been thoroughly milled or not.

### PART 3.—*Effect of Surface-Tension-Reducing Agents on Strengths of Moulding Sands.*

It is known that the green strength of a given sand is increased by continuing the milling. This increase depends on the sand, the maximum being reached more quickly in some cases than in others. By reducing the surface tension of the water added it was thought that the rate of spread would be increased, with a consequent reduction of the milling time necessary to produce the maximum green strength.

A substance with the trade name Perminal was used at the recommended concentration of 0.05% of the charge. A synthetic sand and a naturally bonded sand were investigated; figures showing the green strengths for various milling times and the variation of green strength with moisture content are given in Tables IV. and V.

TABLE IV.—*Effect of Perminal on Green Strength (Different Milling Times).*

Mixture.	Milling Time. Min.	Green Strength. Lb. per sq. in.	Green Strength (Perminal added). Lb. per sq. in.
Arnold 52 sand with 5% P.V.B. ball clay (water content 1.8%)	2	2.31	1.65
	4	2.73	2.17
	6	3.29	1.88
	8	3.55	1.59
	10	2.93	...
Naturally bonded I.M. sand (water content 4%)	2	10.00	10.18
	4	10.74	10.98
	6	10.85	11.48
	8	10.98	10.76

TABLE V.—*Effect of Permal on Green Strength (Different Water Contents).*

Mixture.	Water Content. %.	Green Strength. Lb. per sq. in.	Green Strength (Permal added). Lb. per sq. in.	Dry Strength. Lb. per sq. in.	Dry Strength (Permal added). Lb. per sq. in.
Arnold 52 sand with 5% P.V.B. ball clay	1.2	1.16	...	...	...
	1.5	3.63	1.43	...	...
	1.8	3.50	2.23	...	...
	2.0	...	1.75	...	...
	2.1	2.73	...	...	...
	2.2	...	1.22	...	...
	2.5	1.94	0.85	8.4	8.5
Naturally bonded I.M. sand	3.0	10.10	9.15	...	...
	3.5	10.21	11.30	...	...
	4.0	10.64	10.50	...	...
	4.5	9.80	9.89	...	...
	5.0	8.57	9.81	10.5	12.4

The dry strength at the maximum moisture content used is also given.

The results show that, whereas the maximum strength is reached more quickly when Permal is added, the value is reduced considerably in the case of the synthetic sand; in the naturally bonded sand there is a slight increase. A variation in the moisture content producing the maximum green strength is also shown, and the value of this is much decreased in the synthetic sand.

#### PART 4.—*The Permeability of Moulding Sands.*

##### (a) *Introduction.*

The permeability of moulding sands is of direct importance in foundry work. For instance, the rate of drying of dry-sand moulds, under a given set of conditions, is governed mainly by the permeability of the sand. Fig. 6 shows the difference in the rates of drying of test-pieces of A.F.A. dimensions prepared from two mixes containing the same proportions of moisture; the first mix was composed of Arnold's No. 52 sand bonded by the addition of 10% of ball clay, while the second was a naturally bonded sand from Tow Law, County Durham. After 15 min. drying at 200° C. the Arnold's test-pieces lost 84% of their total moisture, while the Tow Law test-pieces lost only 54%. After 90 min. the Arnold's pieces were completely dry, while the Tow Law pieces were still losing moisture. The permeability coefficient of the Arnold's test-pieces was 180, whilst that of the Tow Law test-pieces was 14.

The measurement of permeability has other applications. Thus, the strength of both green-sand and dry-sand moulds and the



extent to which a core sand can accommodate the contraction of a casting during cooling are all closely related to permeability.

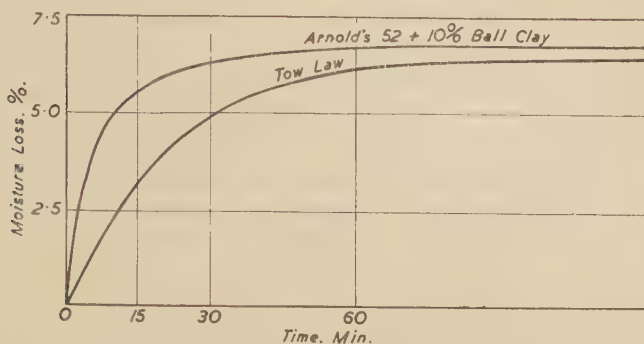


FIG. 6.—Drying Rates of Two Mixes.

### (b) The Determination of Permeability.

The British Cast Iron Research Association air permeability apparatus, shown in Fig. 7, has several disadvantages. The chief of these is that the pressure in the air reservoir is not constant; on the contrary it depends on the permeability of the test-piece. Whether the pressure of the air passed through the test-piece is measured by a manometer attached to the pipe-line between the reservoir and the test-piece holder or is connected separately to the holder, it does not record the pressure of the air in the reservoir. The air pressure in the reservoir is higher than the recorded pressure owing to the resistance of the pipe-line; this resistance is a variable depending on the rate of flow of the air through the pipe, and therefore on the permeability of the test-piece. Furthermore, the rate of sinking of the reservoir depends not only on the permeability of the test-piece, but on the resistance due to the viscosity of the water in the reservoir and to the friction between the sliding tubes in it; that is, the pressure in the reservoir is also governed by the rate of sinking of the reservoir. Consequently, in the permeability test, 2 litres of air, at an unknown pressure (higher than the manometer reading), are passed through the test-piece; since this unknown pressure depends on the permeability of the test-piece, it follows that the time for the passage of 2 litres of air is not a measure of the mass of air passed through the test-piece.

The importance of the pipe-line and reservoir resistances increases as the permeability of the test-pieces is increased. For instance, a test-piece of Arnold's 52 sand bonded with 2.5% of ball clay required 15 sec. for the passage of 2 litres of air, while a test-piece of a close rotten rock required 350 sec. When no test-piece was used, 2 litres of air escaped from the reservoir in 10 sec.

It has been the practice to add weights to the reservoir so that

the manometer reading shall be constant at 10 cm. of water. Usually a considerable load must be added for a test-piece of Arnold's 52 sand, and little or no load for a rotten-rock test-piece. The additional load for the Arnold's test-piece is necessary because of the rapid flow of air and the consequent high resistances developed by the pipe-line and by the sinking of the reservoir. In the case of the rotten rock, the flow of air is slow, and the resistances developed by the apparatus are slight. In other words, if the manometer reading is to be constant, the air pressure in the reservoir must be higher for the Arnold's test-piece than for the rotten-rock test-piece. Hence the mass of air passed through the test-piece is varied according to the permeability of the test-piece.

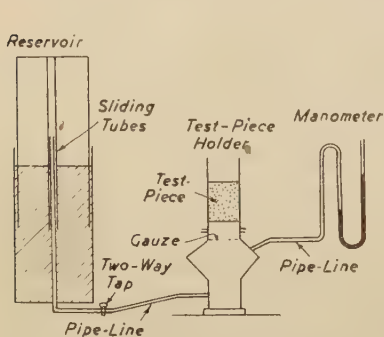


FIG. 7.—British Cast Iron Research Association Air-Permeability Test Apparatus.

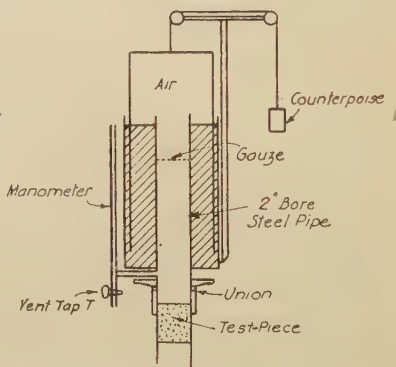


FIG. 8.—Modified Permeability Test Apparatus.

*Modified Permeability Apparatus.*—To overcome this difficulty, a modified form of permeability apparatus was designed, as shown in Fig. 8. In this form, the reservoir floats on water and is maintained in an upright position by means of a small counterpoise. The outlet from the reservoir is made of steel pipe, having a bore of 2 in. and a length of more than six diameters; a disc of wire gauze is fitted in the pipe at a distance of two diameters from the top. By this means the air flow is rendered uniform over the whole of the cross-section near the bottom of the pipe, that is, at the point where the pressure is measured. The test-piece is rammed in a short length of pipe of 2-in. bore and attached to the outlet pipe by means of a union; the joint is made air-tight by a rubber washer.

In operation, the lower end of the test-piece holder is closed by a glass plate coated with vaseline. The vent tap *T* is opened, the reservoir raised and the tap closed. The level of the reservoir is then observed to see that there are no leaks. Provided that there are none, the glass plate is slipped off, and the time for the passage of 1 litre of air and the manometer reading are noted. The

pressure when the glass plate is in position is 7.35 cm.; this falls to 7.2 cm. when the plate is removed, and this value is independent of the permeability of the test-piece. Furthermore, if the empty test-piece holder is used, the reservoir discharges instantaneously on the removal of the glass plate. Thus the resistances due to the pipe-line, friction and viscosity are negligible.

A comparison was made between the permeability determinations by the B.C.I.R.A. apparatus and by the modified apparatus. The test-pieces were made from the following mix :

Chelford Sand.	Wyoming Bentonite.	Water.
100%	+1.5%	+1.75%

The height of the test-pieces was varied, but the ramming density was constant. The time for the passage of air in the modified apparatus was doubled to correspond to the 2 litres passed in the B.C.I.R.A. apparatus. The results are shown in Table VI. For

TABLE VI.—*Comparison of B.C.I.R.A. and Modified Permeability Apparatus.*

Height of Test-Piece, H. In.	Modified Apparatus.			B.C.I.R.A. Apparatus.		
	Pressure, P. Cm. of water.	Time, T. Sec.	PT/H.	Pressure, P. Cm. of water.	Time, T. Sec.	PT/H.
2.0	7.2	39.00	140	8.25	28.25	117
1.5	7.2	28.50	137	7.75	23.25	120
1.0	7.2	19.50	140	7.25	19.50	141
0.5	7.2	10.00	144	5.50	14.00	154

the modified apparatus, the factor  $PT/H$  is a constant within the limits of experimental error. Hence the rate of flow of air at constant pressure through a column of sand is proportional to the height of the column, a result which is in accord with the extensive researches of M. Muskat and H. G. Botset.<sup>1</sup> The B.C.I.R.A. apparatus gave a factor varying from 117 to 154, a far greater difference than can be explained by the experimental error.

*Wologdine's Expression for Permeability.*—The permeability number  $P$ , according to Wologdine,<sup>2</sup> is given by the expression :

$$P = \frac{v \cdot h}{p \cdot a \cdot t},$$

where  $v$  = volume of air passed, in ml.

$h$  = height of specimen, in cm.

$p$  = pressure during experiment, in cm. of water.

$a$  = cross-sectional area of test-piece, in sq. cm.

$t$  = time, in min.

<sup>1</sup> "Flow of Gas through Porous Materials," *Physics*, 1931, vol. 1, July.  
p. 27.

<sup>2</sup> *Stahl und Eisen*, 1909, vol. 29, p. 1221.

If  $v$  and  $a$  are constant, as was the case in the observations recorded in Table VI., then, for a sand at constant bulk density, the factor  $PT/H$  should be a constant. This is true of the modified apparatus but not of the B.C.I.R.A. apparatus. It is therefore suggested that comparisons of permeability should be made by means of the modified form of apparatus. Only then will the permeability of a sand be proportional to its permeability number. To avoid confusion with the *permeability number* determined by means of the B.C.I.R.A. apparatus, the values determined by the modified apparatus may well be referred to as *permeability coefficients*.

Muskat and Botset (*loc. cit.*) showed that the mass-velocity ( $\rho v$ ) of air flowing through sand is related to the difference between the squares of the pressures,  $p_1, p_2$ , at the opposite ends of the test-piece by an equation of the form :

$$(p_1^2 - p_2^2) = k(\rho v)^n,$$

where  $k$  and  $n$  are constants characteristic of the sand. Hence :

$$(p_1 - p_2)(p_1 + p_2) = k(\rho v)^n.$$

If  $P$  is atmospheric pressure and  $\delta p = p_1 - p_2$ , then :

$$\delta p[2P + \delta p] = k(\rho v)^n.$$

Since the pressures commonly employed in permeability determinations (usually 10 cm. of water) are small compared with atmospheric pressure :

$$2P \cdot \delta p = (\rho v)^n,$$

within the limits of experimental error. Furthermore,  $n$  is but slightly greater than unity, so the rate of flow is nearly proportional to the difference in pressure between the ends of the test-piece, as is assumed in Wologdine's expression. Hence the product of the pressure difference and the time taken for the passage of a given volume of air should be a constant. Observations, such as those below, justify this assumption when the modified apparatus is used :

Pressure, $P$ .	Time, $T$ .	$P \times T$ .
10.3	9.5	95.2
7.2	13.25	95.4

### (c) Factors Influencing the Permeability Coefficient.

A series of tests were made in order to indicate some of the factors influencing the permeability of moulding sands.

(i) *Ramming Density*.—When comparing the permeability coefficients of two sand mixes it is obvious that they must be rammed to the same extent. The following observations were made on test-pieces of A.F.A. dimensions made from a typical green-sand mix :

No. of blows of rammer .	3	9	15	20	30	40
Apparent density .	1.55	1.61	1.63	1.65	1.67	1.69
Permeability coefficient .	185	148	134	122	107	94

The apparent density increases sharply as the number of blows is increased from 3 to 9; further blows of the rammer increase the

density slowly. Correspondingly, the permeability coefficient decreases sharply at first and then slowly.

When the tests are repeated on fresh test-pieces, the permeability coefficients agree more closely for 9 blows than for 3 blows. Furthermore, the higher density is more nearly comparable with foundry practice. It is therefore suggested that for comparisons of permeability, the test-piece should be given 10 blows of the rammer.

(ii) *Moisture Content and Bond Content.*—The results of permeability determinations on a series of mixes of Chelford sand and Wyoming bentonite are shown graphically in Fig. 9. The per-

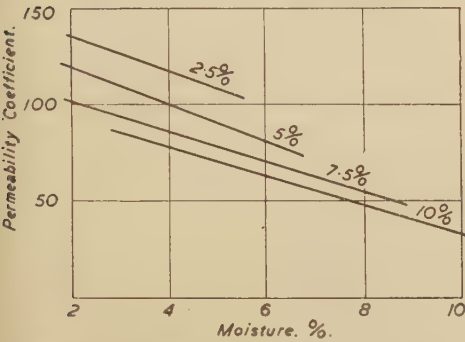


FIG. 9.—Permeability Results for Chelford Bentonite Mixes.

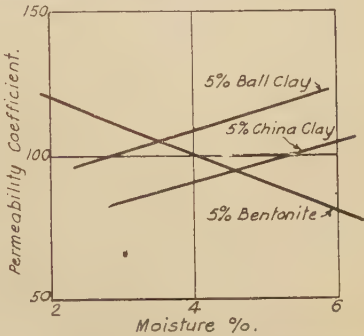


FIG. 10.—Variation of Permeability Coefficient with Moisture Content of Mixes of Chelford Sand with Ball Clay, China Clay and Bentonite.

meability coefficient decreases as the moisture content increases; this is because the bentonite swells and fills the pores. For a given moisture content, the greater the bond content, the lower is the permeability coefficient, as might be expected.

(iii) *Nature of Bond.*—When bentonite mixes are employed, the permeability coefficient decreases as the moisture content increases; this is not true of ball-clay or china-clay mixes. Fig. 10 indicates the variation in the permeability coefficient with moisture content for china clay, ball clay and bentonite, respectively. The permeability coefficients of both the china-clay and the ball-clay mixes increases slightly as the moisture content increases.

PART 5.—*Thermal Expansion of Sand Mixtures Containing Clays.*

The expansion of sand mixtures on heating is a factor of some significance in steel-foundry practice, and it was decided to carry out experiments to discover whether there was any important difference in the rate of expansion on heating and the final expansion reached when sand mixtures were made up with different types of clay. The results of three such experiments are shown in Fig. 11.



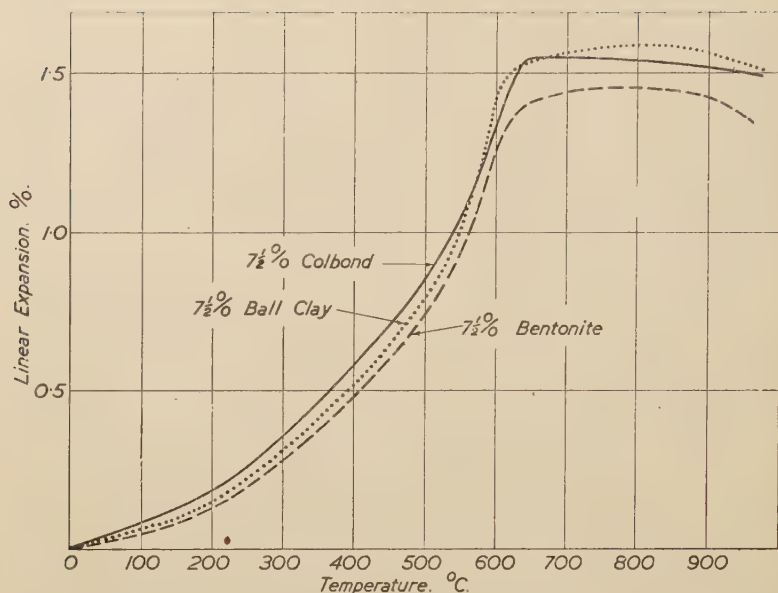


FIG. 11.—Thermal Expansion Curves for Mixtures of Arnold's 52 Sand and Clay.

Mixtures were made of Arnold's 52 silica sand with additions of  $7\frac{1}{2}\%$  of bentonite, Colbond and ball clay, respectively. Thermal expansion test-pieces were moulded and all the specimens were dried at  $200^{\circ}\text{C}$ . for 2 hr.

Thermal expansion tests were then carried out, the rate of heating in the range between  $200^{\circ}$  and  $700^{\circ}\text{C}$ . being  $2^{\circ}\text{C}$ . per min. in each case. The highest expansions recorded in each test were as follows :

	Expansion.
$7\frac{1}{2}\%$ Colbond . . .	1.55%
$7\frac{1}{2}\%$ ball clay . . .	1.59%
$7\frac{1}{2}\%$ bentonite . . .	1.46%

Although the expansion of the mixtures containing Colbond and ball clay is somewhat greater than that of the mixture containing bentonite, the difference is not great, and it is doubtful whether differences of this order will have any significant effect on the behaviour of sands containing the different clays in actual use in the foundry.

#### PART 6.—The Use of "Insulating" Sands.

In the course of one of their investigations the Foundry Practice Sub-Committee discovered that improved feeding in certain types of head resulted from the use of a head lining with a low thermal

TABLE VII.—*Thermal Conductivities of Insulating Mixtures.*

The coke, sawdust, foamed slag and firebrick in mixtures Nos. 3 to 8 was screened to pass a B.S.I. No. 8 sieve and remain on a No. 22 sieve. The firebrick in mixture No. 10 was screened to pass a B.S.I. No. 10 sieve and remain on a No. 16 sieve. The Arnold 52 sand was used as received, except in mixture No. 11, for which it was screened to pass a B.S.I. No. 12 sieve and remain on a No. 24 sieve.

No.	Composition.	Hot Face. ° C.	Cold Face. ° C.	Air Temp. ° C.	Thickness. cm.	Heat Loss. Cal. per sq. m. per hr.	Mean Temp. ° C.	Thermal conductivity.	Estimated Porosity. %
1	Arnold 52 10% P.V.B. ball clay	859	182	25	7.5	2917	516	$\left\{ \begin{array}{l} 0.0091 \text{ c.g.s.} \\ 2.64 \text{ B.Th.U.} \end{array} \right\}$	35-40
2	Arnold 52 25% resin 10% P.V.B. clay	Impossible to make brick satisfactorily. At a drying temperature of 100° C. the brick shrank badly and approached collapse.					...	...	...
3	Arnold 52 35% coke (-8, +22) 10% P.V.B. clay	510	117	20	7.6	1439	314	$\left\{ \begin{array}{l} 0.0067 \text{ c.g.s.} \\ 2.23 \text{ B.Th.U.} \end{array} \right\}$	4-45
4	Arnold 52 50% coke (-8, +22) 10% P.V.B. clay	699	168	23	6.5	2600	433	$\left\{ \begin{array}{l} 0.0088 \text{ c.g.s.} \\ 2.55 \text{ B.Th.U.} \end{array} \right\}$	35-40
5	Arnold 52 25% sawdust (-8, +22) 10% P.V.B. clay	423	78	19	7.6	750	250	$\left\{ \begin{array}{l} 0.0046 \text{ c.g.s.} \\ 1.33 \text{ B.Th.U.} \end{array} \right\}$	65-70
6	Arnold 52 50% sawdust (-8, +22) 10% P.V.B. clay	480	78	20	4.5	715	279	$\left\{ \begin{array}{l} 0.0023 \text{ c.g.s.} \\ 0.67 \text{ B.Th.U.} \end{array} \right\}$	7-80
7	Arnold 52 25% foamed slag (-8, +22) 10% P.V.B. clay	756	142	19	7.5	1918	449	$\left\{ \begin{array}{l} 0.0065 \text{ c.g.s.} \\ 1.89 \text{ B.Th.U.} \end{array} \right\}$	45
8	Arnold 52 50% porous firebrick (-8, +22) 10% P.V.B. clay	669	144	23	7.3	1943	406	$\left\{ \begin{array}{l} 0.0074 \text{ c.g.s.} \\ 2.2 \text{ B.Th.U.} \end{array} \right\}$	40-45
9	100% coke dust	941	272	24	4.5	6032	606	$\left\{ \begin{array}{l} 0.0011 \text{ c.g.s.} \\ 3.19 \text{ B.Th.U.} \end{array} \right\}$	35-40
10	Crushed firebrick 15% P.V.B. clay	457	9	18	7.8	1020	275	$\left\{ \begin{array}{l} 0.0061 \text{ c.g.s.} \\ 1.79 \text{ B.Th.U.} \end{array} \right\}$	45-50
11	Arnold 52 15% P.V.B. clay	603	120	10	7.69	1500	362	$\left\{ \begin{array}{l} 0.0067 \text{ c.g.s.} \\ 1.94 \text{ B.Th.U.} \end{array} \right\}$	...

conductivity, and asked for the examination of "insulating" mixtures to be carried out by the Moulding Materials Sub-Committee. Table VII. gives the thermal conductivities of a number of the mixtures tried. It will be noticed that the mixtures with the lowest thermal conductivity are Nos. 5 and 6 containing sawdust, and this type of material, made up of a silica sand, sawdust and clay, was subsequently found by the Foundry Practice Sub-Committee to give the most satisfactory results when used for lining feeder-heads.

#### PART 7.—*Conclusion and Recommendations.*

It will be noticed that the sands examined occur in widely separated parts of Great Britain. It is suggested that, in view of present transport difficulties, which are always liable to increase considerably during the winter months, foundries should carry out trials more particularly of sands which occur reasonably near at hand.

The point must be emphasised that many naturally bonded sands do not yield their full strength on milling unless the rolls are sufficiently heavy and the time of milling is sufficiently long. The weight of the rolls should be the maximum which can be used without actually crushing the sand grains. The time of milling should be sufficiently long to distribute the clay uniformly over all the sand grains present, including those of the silica sand which is frequently used to dilute a heavily bonded natural sand.

The use in lining feeder-heads of mixtures with a low thermal conductivity is decidedly advantageous as far as feeding is concerned, but some care is necessary to ensure that this material, containing a large percentage of sawdust, does not become mixed with the ordinary backing sand when knock-out sand is being recovered for re-use.

### SECTION III.—CLAYS.

#### PART 1.—*The Use of Fullers' Earth in Steel Foundries.*

During the years immediately preceding the present war, the manufacture of steel castings in green sand made rapid and considerable progress. A large part of this expansion was associated with the use of synthetic sands, in which the mixtures for moulding were prepared from domestic silica sands and the natural clay bentonite, which was imported from the United States of America. Apart from an increase in the number of small repetition castings, there was an extension in the variety of types, and an increase in the maximum size and weight of castings made in green moulds. Other

castings, in some cases of larger size, were made in skin-dried moulds, the sand mixture often consisting of silica sand and bentonite, with a small addition of an organic material, usually of the dextrin type. In some foundries, bentonite was regularly used as an additional clay in the facing sand for dry-sand moulds. Another, smaller, use of bentonite was as a constituent of mould paints.

The increasing popularity of bentonite in steel foundries was due to a number of causes, the more important of which are briefly as follows. Bentonite is a highly plastic clay, and readily gives moulding mixtures which can be deeply moulded without cracking or breaking away. These mixtures are substantially free from the defect of drying-off and giving a friable surface, to which most similar mixtures containing domestic clays are prone. When a clay is heated to a sufficiently high temperature, it does not readily absorb water again on cooling. This permanent dehydration begins at a higher temperature for bentonite than for most domestic clays with a kaolin base. Probably associated with this is the fact that the foundry life of mixtures containing bentonite is long, that is, the sand knocked out of moulds after casting can be used again a considerable number of times with only a small amount of additional new clay each time the sand is re-used. The high green strength of bentonite mixtures means that adequate green strength for moulding can be secured with a small clay content, so that the permeability of the sand is not seriously reduced. Bentonite has an extremely small particle size, so that neither long nor heavy milling is required to give a thorough mixture with a sand and to secure the full bonding value of the clay used.

Bentonite consists essentially of a montmorillonite mineral containing sodium, which is the active constituent, and  $\alpha$  quartz, which is merely a diluent. No deposits of bentonite occur in Britain. Fullers' earth, of which substantial beds in this country have been worked for several hundred years, is, however, a comparable material, consisting substantially of a montmorillonite mineral containing calcium, with calcium carbonate as diluent. Most of the other British clays contain as their active constituent kaolinite, which is less efficient as a binder in green-sand/clay mixtures than montmorillonite. It is, however, considerably more refractory than minerals of the montmorillonite type.

After exhaustive laboratory and foundry trials, it was found that, as far as green-sand moulding was concerned, fullers' earth offered the best practical substitute of domestic origin for imported bentonite, and the Sub-Committee invited the co-operation of the Fullers' Earth Union, Ltd., in surveying the available resources of fullers' earth, in the production of fullers' earth in a form suitable for foundry use, and in carrying out experiments to increase its bonding efficiency by varying the methods of preparation. This co-operation was willingly given, and the Members of the Sub-Committee are greatly indebted to Mr. R. H. S. Robertson for his

valuable assistance in this connection. It was decided that the Fullers' Earth Union, Ltd., should supply these fullers' earths to foundries under the name of Fulbond, several varieties of which are now available.

The initial trials were carried out with Fulbond No. 1, a natural fullers' earth dried and ground under controlled conditions, and with Fulbond No. 2, for which the method of preparation was modified to obtain greater strength. The structures of Wyoming bentonite, Fulbond No. 1 and other materials for comparison are shown as X-ray photographs in Fig. 12. The method of preparing Fulbond No. 2 was subsequently modified further, and as a result Fulbond No. 3 is now regularly supplied to foundries where its special properties are found to be of value. Fulbond No. 1A, like Fulbond No. 1, is a natural fullers' earth prepared and ground without subsequent treatment, but is not obtained from the same deposits as Fulbond No. 1. The kinds of Fulbond now available commercially are thus Nos. 1, 1A, 2 and 3.

Fulbond No. 1 has been found suitable for most steel foundries. In green-sand mixtures its bonding efficiency is 70–80% of that of average Wyoming bentonite, so that in changing from a synthetic sand mixture containing 3% of bentonite, from 4 to 5% of Fulbond No. 1 is required instead. The introduction of this greater percentage of clay naturally decreases to some extent the permeability of the sand mixture. This reduction is usually not important, but if in a particular case the permeability is reduced to too low a figure, the addition of a coarse silica sand, such as Arnold 52 or Leighton Buzzard No. 9, will increase the permeability to the desired figure. If a sand-reclamation system is in operation, it is to be remembered that an additional weight of clay is being carried in the system.

To obtain the full bonding power from Fulbond No. 1, heavier milling and frequently longer milling times are required than with bentonite. Good plastic mixtures which will admit of deep moulding are obtained in this way, and they do not dry off unduly. The foundry life of Fulbond No. 1 in repeated use is comparable with that of bentonite, but slightly shorter. The refractoriness of Fulbond No. 1 is lower than that of bentonite, but the stripping properties of similar mixtures containing each clay are very similar.

The dry strength of sand mixtures containing Fulbond No. 1 is substantially lower than that of similar mixtures containing the same percentage of bentonite, dried under the same conditions. This difference still exists, but is very greatly reduced, when the percentage of Fulbond No. 1 is increased until the Fulbond mixtures have the same green strength as the bentonite mixtures. The manufacture of medium-sized steel castings in skin-dried moulds was increasing at the outbreak of war, and for this purpose mixtures containing bentonite had become popular. This method of making steel castings is probably of greater importance under present conditions, since the only practicable way of avoiding it is by the installation



of additional drying stoves, for which there is usually little space available. For this purpose mixtures of silica sand and Fulbond No. 1 alone have not proved entirely satisfactory. The addition to such mixtures of an organic material, such as a small amount of dextrin or G. B. Kordek, is of great practical advantage and gives satisfactory results in nearly all cases. It is generally unnecessary for the organic addition to exceed 1% of the weight of the mixture.

For the manufacture of dry-sand steel castings, naturally bonded sands have always been much more widely used than silica-sand/bentonite mixtures, and mixtures of silica sand with fullers' earth are similarly of relatively minor importance. During the present emergency it has been necessary to extend the use in steel foundries of clays of British origin. Many of these, when used in proportions which give mixtures with adequate dry strength, do not provide sufficient green strength, and in some cases give mixtures which are not sufficiently plastic to mould deeply without cracking or breaking. In such sand mixtures, the addition of Fulbond No. 1 in proportions up to 20% of the total clay content improves the mixtures considerably in both respects and enables satisfactory moulds to be made.

Fulbond No. 1A, like Fulbond No. 1, is a naturally occurring fullers' earth, dried and ground under controlled conditions, but not specially treated in any other way. In properties it is generally similar to Fulbond No. 1, but develops slightly less strength.

Fulbond No. 3 is a fullers' earth which has been treated chemically in order to increase the green strength of mixtures containing it. When milled with silica sand it develops its maximum green strength more quickly than Fulbond No. 1 and permits of a reduction in the weight of the rollers or of the milling time. The variation of green strength with the moisture content of the mixture is more rapid with Fulbond No. 1 than with bentonite. Similar mixtures containing Fulbond No. 3 are considerably less sensitive to variations in water content, and in this respect Fulbond No. 3 approaches bentonite in its properties.

A comparison of the green strengths of mixtures made in the laboratory by milling a coarse-grained silica sand with the same proportion of Fulbond No. 1 and Fulbond No. 3 is given in Table VIII. This shows the superior green strength of the Fulbond No. 3 mixtures, also that this green strength falls off with increasing water content more slowly than that of the Fulbond No. 1 mixtures, and, further, that the dry strength of the Fulbond No. 3 mixtures is greater than that of the corresponding Fulbond No. 1 mixtures. The extra chemical treatment given to Fulbond No. 3 makes its price higher than that of Fulbond No. 1. It has been found in practice that Fulbond No. 1 gives quite satisfactory results, and there is no need to obtain the more expensive Fulbond No. 3, except in cases where its special properties can be advantageously employed.

TABLE VIII.—*Arnold's 52 Silica Sand with 5% of Fulbond No. 1 and with 5% of Fulbond No. 3.*

Test cylinders 2 in. × 2 in. rammed in A.F.A. apparatus; number of blows, 10. Specimens dried at 200° C. for 2 hr.

Water Content. %.	A.—5% of Fulbond No. 1.		B.—5% of Fulbond No. 3.	
	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
1.25	8.4	...	11.45	15.9
1.50	8.0	12.7	10.20	21.0
1.75	7.0	17.5	8.95	21.6
2.00	6.6	18.7	8.75	23.2
2.50	5.9	22.0	7.95	27.6
3.00	5.25	25.2	7.47	33.0
3.50	4.15	32.8	7.25	41.0
4.00	3.26	38.9	7.16	47.0

TABLE IX.—*Chelford Silica Sand with Bentonite and with Fulbond.*

Test cylinders 2 in. × 2 in. rammed in A.F.A. apparatus; number of blows, 10. Samples dried at 230° C. for 2½ hr.

Clay Addition.		Permeability No.	Water Content. %.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
Bentonite	3%	119	3.5	5.5	55
	3%	99	5.0	5.0	85
	4%	105	3.6	6.6	65
	4%	99	5.0	6.1	100
	5%	93	3.5	8.6	100
	5%	88	5.1	7.5	115
Fulbond No. 1	3%	119	3.5	2.7	33
	3%	99	5.2	1.6	52
	4%	105	3.6	4.5	55
	4%	99	5.0	2.8	61
	5%	105	3.6	6.6	65
	5%	93	5.2	4.3	96
Fulbond No. 3	3%	115	3.6	3.9	43
	3%	105	5.2	3.1	61
	4%	108	3.6	5.3	54
	4%	99	5.2	4.0	80
	5%	105	3.5	7.3	90
	5%	93	5.2	5.5	105

The properties of mixtures made from a silica sand of medium grain size with 3, 4 and 5% of bentonite, Fulbond No. 1 and Fulbond No. 3 are given in Table IX. The results in Tables VIII and IX. must be regarded as typical and of comparative value only, since the sands and clays used are natural products, subject to some variation in properties in different parts of the deposits from which they are derived.

A number of steel foundries paint moulds with a creamy liquid

consisting essentially of silica flour suspended in water, thickened by the addition of sulphite lye, core cream or other organic material. The addition of bentonite to these liquid paints gave improved results, since the bentonite helped to keep the silica flour in suspension, and also assisted in hardening the paint on drying. For this purpose bentonite may be replaced by either Fulbond No. 1, No. 2 or No. 3. In such paints Fulbond No. 2 is most effective, and No. 3 is better than No. 1, but if a foundry uses Fulbond No. 1 for other purposes it is scarcely worth while obtaining a supply of Fulbond No. 2 or No. 3 merely for making up paints.

TABLE X.—*Chelford Silica Sand with A.C.33.*

Test cylinders 2 in. × 2 in. rammed in A.F.A. apparatus; number of blows, 10. Samples dried at 230° C. for 2½ hr.

Clay Addition. %.	Permeability No.	Water Content. %.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
3	112	3.4	4.0	42
3	102	5.25	2.5	52
4	112	3.5	4.6	47
4	93	5.1	3.6	77
5	102	3.4	7.1	55
5	96	5.2	5.1	83

TABLE XI.—*Sand Mixtures used in the Foundry.*

Base sand : Yorkshire, 25%; Chelford, 75%.

Test cylinders 2 in. × 2 in. rammed in A.F.A. apparatus; number of blows, 10. Samples dried at 230° C. for 2½ hr.

Clay Addition.		Permeability No.	Water. %.	Green Strength, Lb. per sq. in.	Dry Strength, Lb. per sq. in.
Bentonite	3%	77	3.75	13	100
Fulbond No. 1	5%	65	4.0	14	115
Fulbond No. 3	4%	73	3.9	11	90
A.C.33	4%	65	4.2	10	110

Another material of the fullers' earth class is marketed under the name "A.C.33." The properties of sand mixtures made with Chelford silica sand and different percentages of A.C.33 are shown in Table X. Comparing these with the results in the previous Tables, the binding properties of A.C.33 are superior to those of Fulbond No. 1 and are very close to those of Fulbond No. 3. Like Fulbond No. 3, A.C.33 has a longer range of useful moisture content than Fulbond No. 1. Table XI. gives the properties of sand mixtures prepared in a foundry pan-mill, using as the base sand a mixture containing 25% of Yorkshire moulding sand with 75% of Chelford silica sand, the additional binders being bentonite, Fulbond No. 1,

Fulbond No. 3 and A.C.33. The properties of the resultant mixtures are all very similar, and all were used for making the same type of green-sand casting. All the mixtures moulded well and the moulds had a good surface, although the mixture containing A.C.33 was a trifle sticky and had a tendency to ram to a joint. All the castings stripped well and there was no significant difference between their surfaces.

Samples of other clays of the fullers'-earth group are being examined by Members of the Sub-Committee, and where the results of laboratory investigations are sufficiently promising foundry trials will be arranged.

### *Conclusion and Recommendations.*

The clays of domestic origin which have properties nearest to those of bentonite are of the fullers'-earth type, and a large number of steel foundries formerly using bentonite are now using fullers' earth instead with good results. In most cases Fulbond No. 1 has proved satisfactory. Less satisfactory results are often due to the use of insufficiently heavy mills or to an inadequate time of milling. If heavier or longer milling cannot be carried out, it is advisable to use Fulbond No. 2 or No. 3 instead of Fulbond No. 1. Where very high dry strengths are required, some of the leaner domestic clays can be used with advantage, the necessary green strength being obtained by an addition of Fulbond No. 1. Particular examples of this are given in a later Section of this Report.

One point to be remembered is that the foundry life of fullers' earth appears to be slightly less than that of bentonite. As, in any case, the clay content of mixtures using fullers' earth is higher than that of mixtures with similar strengths containing bentonite, it is very advisable to make sure, if recovery or reclamation of moulding sand is being carried out, that a sufficiently high proportion of old clay or old sand is removed and new clay added. Neglect of this precaution may lead to trouble in stripping or other defects on the surface of the castings.

## PART 2.—*Report on Clays other than Fullers' Earth.*

(Fig. 12 = Plate XXXIX.)

A considerable number of clays have been fully investigated, and the trials show that some of them, selected ball clays in particular, when used in proportions of 5–10% with a silica sand give satisfactory green strength, but are lower in dry strength than normal Fulbond or bentonite mixtures. The kaolinite-clay-bonded sands have a greater hot strength than the Fulbond or bentonite mixtures, and in some branches of foundry work this is a definite advantage.

The fundamental investigation of the characteristics of bond

clays and of the mechanism of bonding is continuing; the results obtained confirm the superior bonding power of clays of the montmorillonite type. Apart from the fullers' earths, the only clays occurring in Britain so far found to contain much montmorillonite are those occurring in the London Clay measures, but they also contain a high proportion of siliceous silt, which lowers their bonding power. The bond strength, dry-strength/green-strength ratio, and range of retention of green strength with increasing moisture content of these montmorillonite-containing materials varies directly with their montmorillonite content. An interesting example of the occurrence of montmorillonite is in a silty clay which is recovered from the washing of the sand used for sand-lime brick-making at Sevenoaks, Kent. This reclaimed clay has useful bonding power, but its montmorillonite content is too low to put it into the fullers'-earth class.

The following records of experimental investigations and practical trials cover a number of alternative bond materials, which have been examined by the Members of the Sub-Committee.

### *Colbond.*

This is a finely ground plastic clay imported from Eire. It is a useful material, giving good moulding properties to the sand.

Comparison of the properties of sand mixtures made up with Arnold's No. 52 sand, bentonite, fullers' earth and Colbond are shown in Table XII.

TABLE XII.—*Mechanical Tests on Mixtures with Arnold's No. 52 Sand as Base.*

Sample No.	Composition of Mixture.	Weight of Test-pieces. G.	Moisture. %.	A.F.A. Permeability No.	Green Strength. Lb. per sq. in.	Dry Strength, Lb. per sq. in., dried at—	
						200° C.	400° C.
1	6% Colbond 94% Arnold's No. 52.	160	2.4	420	3.5	61	62
2	5% Colbond 1% Bentonite 94% Arnold's No. 52.	160	2.6	420	5.1	90	103
3	6% Fullers' earth 94% Arnold's No. 52.	160	3.6	380	7.2	91	99
4	3% Fullers' earth 97% Arnold's No. 52.	155	2.6	450	3.5	36	40
5	3% Bentonite 97% Arnold's No. 52.	157	2.7	430	3.3	66	61

*Sintering Characters.*—A.F.A. test-pieces all fired together to 1500° C., had the characteristics stated in Table XIII.



TABLE XIII.—*Character of Sintered Test-Pieces, After Firing at 1500° C.*

Sample No.	Composition of Mixture.	Expansion after Firing.			Crushing Strength when Cold. Lb. per sq. in.
		Diameter. In.	Length. In.	Volume Increase. %.	
1	6% Colbond + 94% Arnold's No. 52.	0.07	0.08	11.1	175
3	6% Fullers' earth + 94% Arnold's No. 52.	0.20	0.19	33.0	300
4	3% Fullers' earth + 97% Arnold's No. 52.	0.18	0.14	27.0	170
5	3% Bentonite + 97% Arnold's No. 52.	0.11	0.12	17.8	140

Samples 3, 4 and 5 showed cracks after firing, so that the high apparent expansion is due mainly to the occurrence of cracks.

The refractoriness under reducing conditions of Colbond in comparison with fullers' earth and bentonite is as follows :

Colbond . . . . .	1565–1620° C.
Fullers' earth (Fulbond No. 2) . . . . .	1290° C.
Bentonite . . . . .	1405–1440° C.

It is interesting to note the low refractoriness of the two latter. In spite of this, the crushing strength of the test-pieces fired at 1500° C. is not unduly high.

Further information relating to the properties of Colbond is given below, in the discussion of the properties of Kingscliffe and Sandhurst clays.

Compared with fullers' earth, Colbond is more refractory, but its relative value as a bond in the green state is about one-half that of fullers' earth, *i.e.*, about twice as much Colbond is necessary to give the required workability to the moulding sand. Unless the proportion of Colbond used is high there is a tendency to friability on drying, but this can be corrected by the addition of an organic bond such as G. B. Kordek. This friability is also reduced if a proportion of fullers' earth or bentonite, varying from one-tenth to one-fifth of the weight of Colbond used, is added to the mixture.

#### *Benbond.*

This is a finely ground plastic clay prepared from a deposit in Essex. In general properties as a bond it is comparable with Colbond, and in foundry-sand mixtures it behaves in much the same way. The *chemical analysis* of the clay is as follows :

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on Ignition.
57.2%	7.15%	18.41%	3.1%	2.24%	10.5%

*Mechanical analysis* gave the following results :

Sand grade, 1·4%. Silt grade, 36·4%. Clay grade, 62·2%.

Milled in a laboratory mill with various silica sands in different percentages, and at different water contents, the properties of the sand mixtures are shown in Table XIV. The indications are that a clay content of 7% should prove adequate for normal green-sand purposes.

TABLE XIV.—*Properties of Silica-Sand/Benbond Mixtures.*

Composition of Mixtures. %.		Water. %.	A.F.A. Per-meability No.	Green Strength. Lb. per sq. in.	Dry Strength, dried at 200° C. for 1 hr. Lb. per sq. in.	Remarks.
Sand.	Benbond.					
King's Lynn Red. 95	5	3·4	143	6·3	29	All milled for 14 min.; not plastic and not suitable for moulding.
94	6	3·5	138	8·2	29	
93	7	4·2	138	7·7	35	
92	8	4·3	137	9·3	39	
92	8	5·3	125	5·8	67	
Chelford.						All milled for 10 min. * Suitable for moulding.
94	6	3·0	144	7·2	31	
94	6	4·0	133	4·5	32	
93	7	2·9	125	9·8	22*	
93	7	4·2	120	5·7	56*	
92	8	3·0	120	11·1	32	
92	8	4·1	118	7·6	59*	
91	9	3·0	105	13·1	43*	
91	9	4·0	96	9·1	68*	
90	10	3·0	99	15·5	48*	
90	10	4·0	90	10·5	70*	
Leighton Buzzard No. 9. 92	8	3·5	250	13·0	35	Milled for 10 min.; mould well.
King's Lynn Red. 92	8	4·0	179	12·4	48	
92	8	4·0	137	9·7	91	Too wet.

*Distribond ; and English Clays, Lovering and Pochin Co., Ltd., Clays Nos. 1, 2, 3 and 4.*

In discussing a range of clays containing various proportions of bentonite, it is appropriate at this stage to indicate a series of X-ray studies which have been applied to this group of materials, as well as to bentonite and the fullers'-earth materials.

Recent X-ray studies, summarised by Partridge,<sup>1</sup> have shown that there are two groups of clays. One contains about 40% of alumina and is of the kaolin type ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ); the other contains a higher proportion of silica to alumina, and is represented by the structure of pyrophyllite<sup>2</sup> and montmorillonite ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ).<sup>3</sup> These clays are built up of layers of hydrated silica and alumina. The structure of the individual layers is the same, and the difference between the clays lies in the order and relative proportions in which the layers are piled one on top of the other, and in the sideways shifts of the layers or of the atoms in the layers to produce a position of minimum potential energy.

When water is added to montmorillonite it is absorbed in the form of sheets of water molecules between the sheets of the oxygen atoms of the silica layers, thus lengthening the *c* axis of the crystal, the other axes remaining unchanged.<sup>4</sup> It has been suggested, however, that only the first four molecules of water enter the cell in this way and the remainder becomes attached to the exterior oxygen surfaces of the particles of clay.<sup>5</sup> This water becomes attached to the clay particle and fits into the crystal structure, but the looseness of the attachment allows easy movement of the particles, thus conferring the property of plasticity.

The montmorillonite clay develops greater plasticity and bonding strength when mixed with water than the kaolin type of clay. This has been proved in green-sand foundry practice where bentonite, which consists largely of montmorillonite, has excelled other bonding clays of the kaolin type.

It was considered that an X-ray examination of the various bentonite substitutes would be of interest. The X-ray powder photographs are shown in Fig. 12, and the constitutions of the various bonding materials are summarised in Table XV. In the X-ray photographs the calcite and quartz lines are sharper than those given by montmorillonite, so that the proportions of calcite and quartz appear higher than they really are.

It is evident from the results in Table XV. that Distribond No. 1 is a siliceous clay containing bentonite, while Distribond No. 2 is a siliceous clay mixed with another clay containing montmorillonite. "English clays" Nos. 1 and 2 are mixtures of china clay and bentonite, and "English clays" Nos. 3 and 4 are mixtures of china clay and Fulbond. The amount of kaolinite in Distribond No. 1 and the amount of montmorillonite in "English clays" Nos. 3 and 4 are below the visibility limit of the X-ray. The large amounts of

<sup>1</sup> J. H. Partridge, Cantor Lectures, *Journal of the Society of Arts*, 1939, vol. 87, Jan. 13, p. 227; Jan. 20, p. 255; Jan. 27, p. 283.

<sup>2</sup> L. Pauling, *Proceedings of the National Academy of Science (U.S.)*, 1930, vol. 16, p. 123.

<sup>3</sup> J. W. Gruner, *Zeitschrift für Kristallographie*, 1933, vol. 85, p. 345.

<sup>4</sup> W. F. Bradley, R. E. Grim and G. L. Clark, *Zeitschrift für Kristallographie*, 1937, vol. 97, p. 216.

<sup>5</sup> G. Nagelschmidt, *Zeitschrift für Kristallographie*, 1936, vol. 93, p. 481.

TABLE XV.—*Constituents of Various Bonding Materials.*

Bonding Material.	Mineralogical Constitution.			
	Montmorillonite.	Kaolinite.	Quartz.	Calcite.
Wyoming bentonite .	Large amount.	...	Medium amount.	...
Fulbond .	Medium amount	...	...	Medium amount
Distribond No. 1 .	Small amount	...	Large amount	...
Distribond No. 2 .	Small amount	...	Medium/large	Medium amount
"English Clays" Nos. 1 and 2 .	Small amount	Medium/large	Medium/large	...
"English Clays" Nos 3 and 4 .	...	Medium/large	Medium/large	Small amount

quartz and calcite present in the various substances do not develop plasticity and may be regarded as diluents.

Comparative tests on Distribond-sand mixtures are given in Table XVI.

TABLE XVI.—*Comparative Tests on Distribond Nos. 1 and 2, Bentonite and Fulbond.*

	100% Chelford + Bentonite.			100% Chelford + Fulbond.			100% Chelford + Distribond No. 1.			100% Chelford + Distribond No. 2.		
	3·5	7	10	3·5	7	10	3·5	7	10	3·5	7	10
Bond. % .	1·5	2·75	4·0	1·5	2·75	5·0	3·5	2·5	3·0	1·75	3·0	2·5
Moisture content. %												
<i>Green-Test Results.</i>												
<i>A.F.A. Tests.</i>												
Ramming density	1·50	1·50	1·55	1·50	1·50	1·65	1·55	1·60	1·55	1·55	1·60	1·55
Compressive strength. Lb. per sq. in. .	6·3	9·8	12·5	2·4	6·8	7·3	1·0	6·0	7·3	2·4	7·2	7·3
Permeability No..	250	167	120	204	167	107	250	150	167	214	165	177
<i>B.C.I.R.A. Tests.</i>												
Ramming density	1·6	1·6	1·75	1·6	1·6	1·75	1·6	1·6	1·6	1·6	1·6	1·6
Compressive strength. Lb. per sq. in. .	6·75	10·5	17·0	1·75	7·0	8·75	2·0	6·5	9·0	3·0	9·0	9·5
Permeability No..	205	118	71	115	121	78	223	131	133	232	133	148
<i>Dry-Test Results. Dried for 1 hr. at 170° C.</i>												
<i>A.F.A. shear</i>												
strength. Lb. per sq. in. .	30	48	55	31	46	33	31	39	47	30	34	36
<i>B.C.I.R.A. compres-</i>												
sive strength. Lb. per sq. in. .	120	210	472	120	150	421	123	132	181	115	130	140

English Clays, Lovering, Pochin and Co., Ltd.

The chemical analysis of the four clays is as follows :

		No. 1.	No. 2.	No. 3.	No. 4.
SiO <sub>2</sub> . % .	.	55·32	55·92	55·32	54·64
Fe <sub>2</sub> O <sub>3</sub> . %	.	1·14	1·29	1·57	2·0
Al <sub>2</sub> O <sub>3</sub> . %	.	31·34	30·47	30·63	28·45
CaO. %	.	0·16	0·16	0·48	2·10
MgO. %	.	0·58	0·69	0·65	1·05
Loss on ignition. %	.	10·15	9·73	10·0	11·04

No. 4 has a higher content of iron oxide, lime and magnesia than the other clays. This is probably connected with its better behaviour, as shown below.

Trials of mixtures containing 6, 8 and 10% of the ball clay with Chelford silica sand as base were made. It was found that 6% of clay gave mixtures which were too lean, and 10% gave sticky mixtures. The mixtures containing 8% of ball clay gave the results recorded in Table XVII.

TABLE XVII.—*Mechanical Properties of "English-Clay" /Chelford-Silica-Sand Mixtures.*

Mixture : Clay, 8%; Sand, 92%.

Mixture No.	Water. %.	A.F.A. Per- meability No.	Green Strength. Lb. per sq. in.	Dry Strength.* Lb. per sq. in.	Remarks.
Clay No. 1.					
1A	2.45	84	13.3	21	Too dry. Not plastic; dried test- pieces had poor surface. Too wet.
1B	3.3	97	7.7	51	
1C	3.8	100	5.0	60	
Clay No. 2.					
2A	2.55	99	12.3	21	} Same remarks as for No. 1 clay.
2B	3.55	100	6.2	52	
2C	4.2	95	3.8	62	
Clay No. 3.					
3A	2.55	105	11.5	28	Too dry. Better and somewhat plas- tic; simple type of mould practicable. Plastic, but too wet for green-sand moulding.
3B	3.3	117	7.4	50	
3C	4.1	99	3.8	83	
Clay No. 4.					
4A	2.5	115	11.5	44	} Dry.
4B	2.65	111	11.3	59	
4C	2.95	112	9.5	84	
4D	3.5	114	7.9	100	} Plastic, good adhesion.
4E	4.2	100	3.5	110	

\* Dried for 2 hr. at 200° C.

The data show that a mixture of Chelford sand and clay No. 4 adequately milled and containing 3-3.5% of water could be used for making a variety of foundry moulds.

The content of clay can be reduced to 7% and still give good results, as shown in Table XVIII., using Arnold's No. 52 as the base sand. The relative sintering characteristics are indicated by the compressive tests carried out on samples fired at temperatures up to 1600° C.



TABLE XVIII.—*Mechanical and Sintering Properties of Clay-Sand Mixtures with Arnold's No. 52.*

Sand Mixed with—	Moisture. %.	Permeability No.	Green Strength, Lb. per sq. in.	Compressive Strength, Lb. per sq. in., after Firing at—					
				200° C.	400° C.	1200° C.	1400° C.	1450° C.	1600° C.
7% English Clay :						Collapsed			
No. 1 . . .	3.2	410	5.0	103	80		20	...	260
No. 2 . . .	3.3	390	5.2	98	78		45	...	270
No. 3 . . .	2.8	420	4.7	50	50		100	...	700
No. 4 . . .	3.2	380	5.5	57	49		...	770	550
5% Fulbond No. 1 .	4.2	470	5.6	73	52	93	230	...	300
7% Fulbond No. 1 .	3.8	390	6.9	91	...	180	...	350	370

A practical foundry trial with 7% mixtures of Fulbond No. 1A, "English Clay" No. 2 and "English Clay" No. 4 on a 0.40% carbon steel showed no appreciable difference in the stripping properties of these three materials.

*Kingscliffe and Sandhurst Clays.*

These materials have been compared with Colbond in the series of tests recorded in Table XIX. The mixtures were ground in a laboratory mill. The test-pieces were dried at 200° C. for 1 hr.

TABLE XIX.—*Comparison of Kingscliffe and Sandhurst Clays as Bond.*

No.	Sand. %.	Clay. %.	Bent-onite. %.	Water. %.	Permeability No.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
1	K.L. red, 95	Colbond, 5	...	3.4	143	6.5	43
2	K.L. red, 95	Colbond, 5	1	3.7	158	7.9	58
3	Chelford, 95	Colbond, 5	...	2.2	179	5.0	26
4	Chelford, 95	Colbond, 5	1	2.2	185	8.5	39
5	Chelford, 85	Kingscliffe, 15	...	4.6	97	4.0	83
6	Chelford, 85	Kingscliffe, 15	0.5	4.7	97	5.0	120
7	Chelford, 85	Kingscliffe, 15	1	4.5	109	6.4	108
8	K.L. red, 75	Sandhurst, 25	...	6.0	65	5.7	82
9	K.L. red, 85	Sandhurst, 15	...	4.0	97	4.0	25
10	K.L. red, 85	Sandhurst, 15	1	4.5	104	6.2	112

Mixtures 2 and 4 are plastic and should be successful in the foundry. Kingscliffe is a leaner clay and does not give plastic mixtures. Its very high ratio of dry strength to green strength, however, indicates that it might be worth adding to mixtures where high dry strength is advantageous.

High additions of Sandhurst bond were required before much

green strength was obtained. This material is washed out of Biddulph sand, which suggests that it contains free silica, and its chemical analysis confirms this.

The Kingscliffe clay is available in two varieties, white and yellow, both of which have been tested. The yellow variety is a little stronger as a bond than the white, but at least 15% of either of them is necessary to give sufficient green strength with an average base sand. An interesting feature of this bonding material, however, is the relatively high dry strength that it gives, and it may be useful as an addition to other bonding materials.

The Sandhurst clay becomes very "buttery" when wetted, but its bonding value is low, at least 15% being necessary to give a reasonable green strength with an average base sand.

#### *Silklay.*

This is a finely ground plastic fireclay of high refractoriness. As a bond it is about equal to Colbond for green strength, but gives a lower dry strength. The addition of 10% of Fulbond No. 1 (or bentonite) to the clay used as a bond practically doubles the dry strength and also increases the green strength.

#### *Siolite.*

This material in the ground form was received from the Buckland Sand and Silica Co., Reigate Heath, Reigate. Preliminary experiments showed that the material had not a very high green bonding value, and it was necessary to use 14% of it in order to obtain a mouldable mixture. The chemical analysis was :

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on Ignition.
77.2%	7.15%	8.7%	0.4%	0.62%	5.07%

Siolite is a mixture of clay with fine silica. It is not a substitute for bentonite, but is of the same nature as the Sandhurst clay and might have an application in the replacement of silica flour for closing moulds and similar purposes.

#### *Seconite.*

This is a finely ground plastic clay which in proportions not lower than 6% gives satisfactory green strength with an average sand, but dry test-pieces are friable. The Seconite-sand mixtures are lean and would probably not be satisfactory for general steel foundry use; their properties are, however, improved by the incorporation of a small proportion of Fulbond No. 1 (or bentonite).

#### *Beacon Bentonite Substitute.*

This is a finely ground clay which in proportions not lower than 6-8% with an average silica sand gives satisfactory green strength,

but the mixtures are lean and become rather friable on drying. A straight mixture of this bond with a silica sand would not be suitable in general for green-sand castings, but would be improved both in plasticity and surface hardness on drying by a small addition of Fulbond No. 1 (or bentonite).

#### *Cummingbond.*

This is an intimate mixture of a finely ground fireclay with an organic bond of gum type. It gives a poor green strength with an average silica sand, at least 10% being necessary, but a fair dry strength. The air-drying of these mixtures is slow. It is suggested by the makers that this bond is especially suitable for re-vivifying spent sands, and the tests made suggest that it is the "gum" constituent mainly which gives it value for this purpose.

#### *Sintering Tests.*

The tests on all the above bonding materials have included the firing for 2 hr. at 1550° C. of test-pieces made from mixtures of the bond with Chelford sand and Leighton Buzzard sand in proportions sufficient to give a green strength of 5-7 lb. per sq. in., the A.F.A. test-piece being rammed with 10 blows. With the less refractory bonds there was obvious sintering, but in no case was this such as would be likely to give trouble in casting.

#### *White Clay from Spitewinter, Worrall, near Sheffield.*

After receipt the clay was air-dried and ground to pass through a No. 60 B.S. sieve. The clay was analysed and mixtures made with coarse- and with medium-grained silica sands.

Chemical analysis of the material gave the following results, in which the refractoriness and shrinkage are included :

	Sample dried at 105° C.	Fired Sample.
Silica . . . . .	60.71%	67.25%
Alumina . . . . .	19.84%	21.97%
Iron oxide . . . . .	3.68%	4.08%
Titanic oxide . . . . .	1.08%	1.20%
Lime . . . . .	0.15%	0.17%
Magnesia . . . . .	1.08%	1.20%
Potassium oxide . . . . .	2.44%	2.72%
Sodium oxide . . . . .	1.24%	1.37%
Loss on ignition . . . . .	9.71%	...
	<hr/> 99.93% <hr/>	<hr/> 99.96% <hr/>

Refractoriness : Cone 18, 1500° C.

Shrinkage : Plastic to dry, 7.8% linear.

Dry to 1000° C., 6.8% linear.

Mixtures of the clay with Arnold's 52 and with Chelford silica sand were milled in a laboratory mill. Subsequently test-pieces

containing 7·5% and 10% of the clay with each of these sands were fired at 1500° C. They sintered to a hard product, but showed no fusion or deformation. The properties of the milled mixtures are given in Tables XX and XXI.

TABLE XX.—*Spitewinter Clay with Arnold 52 Silica Sand.*

A.F.A. test cylinder 2 in.  $\times$  2 in.; number of blows, 3.  
Samples dried at 200° C.

Clay. %.	Water. %.	Permeability No.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
5	1·5	430	1·83	...
5	2·0	...	1·73	...
5	2·5	...	1·38	9·9
7·5	1·5	...	3·26	...
7·5	2·0	369	3·74	...
7·5	2·5	...	3·61	...
7·5	3·5	...	2·79	33
10	2·0	...	5·73	...
10	3·0	313	5·99	...
10	4·0	...	4·80	...
10	6·0	...	3·18	50

TABLE XXI.—*Spitewinter Clay with Chelford Silica Sand.*

A.F.A. test cylinder 2 in.  $\times$  2 in.; number of blows, 3.  
Samples dried at 200° C.

Clay. %.	Water. %.	Permeability No.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
5	1·5	...	2·25	...
5	2·0	182	2·68	...
5	2·5	...	2·41	...
5	3·0	...	2·23	33
7½	2·0	...	4·51	...
7½	3·0	170	4·62	...
7½	4·0	...	3·72	...
7½	5·0	...	2·39	66
10	2·0	...	6·01	...
10	3·0	164	6·58	...
10	4·0	...	5·73	...
10	6·0	...	3·58	88

### *P.V.B. Ball Clay.*

A sample of this clay in the ground condition was received from English Clays, Lovering, Pochin, Ltd. Tests were carried out on laboratory mixtures with different silica sands as base, using 5% of the P.V.B. ball clay. The results are shown in Table XXII., in which all the base sands mentioned have clean grains with the exception of K.L. red sand, which has a thin film of adherent clay.

TABLE XXII.—*P.V.B. Ball Clay with Various Silica Sands.*Test cylinders 2 in.  $\times$  2 in.; number of blows, 3.

Samples dried at 200° C.

Base Sand.	Water. %.	Permeability No.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
Gwersylt A.	2	...	2.90	...
	2.5	118	3.08	4.4
	3.5	...	2.15	13.4
Gwersylt B.	2	...	3.48	...
	2.5	80	4.64	6.8
	3.5	...	4.05	21.0
Boam No. 4.	1.5	...	2.44	...
	2.0	166	3.18	5.2
	2.5	...	2.55	6.0
K.L. red.	2.0	176	4.67	3.0
	2.5	...	4.51	5.0
	3.5	...	2.68	7.1
Arnold 52.	1.5	...	3.63	...
	2.1	430	2.73	4.9
	2.5	...	1.94	8.4

*Other Clays.*

The Sub-Committee have examined a large number of British clays. In general, the ball clays are strongest as bonds, but one or two fireclays (especially one occurring near Falkirk) have proved equal to the best of the ball clays. Without exception, the dry-strength/green-strength ratio is lower with clays than with Fulbond (or bentonite), the comparisons being made on mixtures of approximately equal green strength and at optimum moisture content. With a higher moisture content than would be suitable for green-sand work, there is a marked increase in the dry strength of all the clay mixtures. With all the clays examined, the thorough admixture of 10–20% of their weight of Fulbond No. 1 (or bentonite) considerably improved their bonding character, the sand mixtures being more plastic, the dry-strength/green-strength ratio improved and the friability on drying decreased. With one or two of the clays, particularly a plastic kaolin, a mixture with 20% of Fulbond No. 1 (or bentonite) brought about a particularly marked increase in the dry/green strength ratio. The addition of a small proportion of an organic bond is also advantageous. The trials made suggest that such mixtures will be satisfactory for use in many foundries, and will allow the conservation of stocks of bentonite.

The tests show that the most suitable clays are those containing a high proportion of “clay substances” and a low proportion of uncombined silica. It is necessary that the clays should be finely ground and that the milling of the sand mixture should be thorough. Although with superfine grinding of the clay (or air-separated clay) there is some improvement in bonding power, it is doubtful if the



improvement is such as will warrant the cost of this additional process.

*Conclusion and Recommendations.*

The search for British clays which might prove of value for foundry purposes has shown that many such clays occur in quantity in various parts of the British Isles. Following on foundry trials, a number are now in regular use and are giving very good results. The clays differ considerably in the green and dry strengths that they give when milled with silica sand, and also in the ratio of dry strength to green strength. One of the most important points which has emerged during the trials is the great improvement in the properties of such mixtures that can be obtained by using more than one clay in a moulding sand. One example, described above, is the improvement of a mixture of silica sand and ball clay when a proportion of Fulbond No. 1 is added. By selecting suitable clays for such mixtures almost any green strength, dry strength or dry/green-strength ratio required in a foundry can be obtained.

During the preparation of moulding mixtures in which domestic clays act as binder, the importance of sufficiently heavy milling for a sufficiently long time cannot be over-emphasised. In a number of cases unsatisfactory foundry results have been obtained, owing entirely to the lack of appreciation of this point. It is probably even more essential when a mixture of clays is being used instead of a single clay.

When mixtures are prepared in a laboratory for testing, it is usually impracticable to carry out heavy milling, and for this reason moulding-sand mixtures milled in the foundry are nearly always higher in strength than those of laboratory mixtures; this applies to many of the results reported above. Another fact not always appreciated when laboratory results are being considered is that when an A.F.A. test cylinder is prepared by the standard method, using three blows of the rammer, the ramming of the sand is much less than that usually reached in the foundry, to attain which about ten blows of the rammer are necessary. Thus, in actual use in the foundry a mixture will be higher in green strength and dry strength and lower in permeability than the results given in the standard A.F.A. test.

Where new deposits of clay are being developed the bonding properties of these clays are often improved if they are allowed to weather, or are kept in a moist condition, for a few weeks before being used. If this has not been done by the suppliers it should be carried out at the foundry.

## SECTION IV.—CORE COMPOUNDS AND CORE-SAND MIXTURES.

In the foundry, sand mixtures containing clay as the essential binding material are usually termed moulding sands, whilst those containing organic binders are classed as core or oil sands. This nomenclature will be used below, even though some moulds are regularly made in organically bonded sands and cores are made in clay-bonded sands.

Core or organically bonded sand mixtures are used for a variety of reasons, each of more or less importance according to circumstances. Such mixtures are frequently more refractory than sands containing clay binders, so that little "burning-on" takes place. When the casting is poured, the organic binder is quickly burnt out, so that the core offers little resistance to the contracting steel. Both these properties contribute to ease of fettling. The dry strength of core sands is usually much higher than that of moulding sands, and the resistance to erosion by the casting stream is therefore greater when core sands are used. Many core sands contain a proportion of linseed oil or resin, and on standing after baking absorb water vapour less readily than the moulding sand after drying. Apart from the above, the use of core sands often offers local advantages in a particular foundry, depending on its equipment and layout.

Most foundries buy their core compounds mixed ready for use, but a few prefer to buy the individual materials and add them in selected proportions to silica sand in a mill or a mixer.

Various materials used as core binders are briefly described below, and are grouped according to the basis of their utility. This classification is, however, not completely accurate, as some of the materials change on heating in more than one significant property, either simultaneously or successively. The substances most commonly used are nearly all imported into Britain, and many of them have a food value either in the form in which they are used in the foundry or after some kind of treatment. For both these reasons it is essential that these materials be used as economically as possible and that reductions in their consumption be secured wherever practicable. A number of alternative materials are mentioned, many of which are imported and are not available in sufficiently large quantities to be utilised generally. It may be, however, that substances similar in nature or in properties arise as by-products, particularly in some of the new war-time industries. In any such cases the Members of the Sub-Committee would be glad to learn of them, to examine samples and to report on their suitability as constituents of core-binding materials.

*Classification of Core Compounds.**Class 1.*

These substances are solid, or nearly solid, at ordinary temperatures, soften or melt on heating, forming a film round each sand

grain, and solidify on cooling, thus providing some green bond and a fairly good dry bond. The best-known example is probably common resin or colophony. Coal tar, pitch and creosote, or a mixture of these, are materials of domestic origin which are less efficient than resin but have often been used in small percentages. Asphalt, or bitumen, behaves in the same way as resin but is an imported material. Other resinous gums include copal, dammar, elemi, guiacum, mastic and sandarac, the commonest of these being gum copal. All of these are imported and are less plentiful than colophony.

Shellac is an imported resin which, apart from being soluble in alcohols, is soluble in some cheap inorganic alkaline solutions. The green and dry strengths of shellac solutions are, however, low.

During recent years many types of synthetic resins have been developed, such as coumarone, glycerine, formaldehyde, alkyd and vinyl resins. These are soluble in various organic solvents, and the addition of a plasticiser gives solutions which develop both green and dry strength, which, however, is never very high.

Colophony, pitch, tar and creosote can be mixed with a fairly thin mineral oil in order to spread them more easily in the cold. This mineral oil supplies a little green strength, but on heating it substantially disappears. Colophony is soluble in linseed oil, and this solution forms a convenient way of introducing the resin. At the same time the total quantity of linseed oil usually used can thus be reduced. A thick resin oil, which is an industrial by-product, is also available, but its resin content and other properties are very variable.

Colophony and the coal derivatives mentioned are practically insoluble in water, and increase the resistance of the core to absorption of water vapour after baking.

### *Class 2.*

These substances on heating undergo a chemico-physical change, with evaporation of water, and leave a solid residue. The commonest example is molasses, which is the uncrystallisable residue in sugar refining. It has an appreciable green strength, and on heating leaves a solid toffee-like residue which has a fair dry strength. Glucose solutions have similar properties and sometimes occur as industrial by-products.

Another somewhat similar material is sulphite lye, a water solution of the residue produced in some processes of the manufacture of wood pulp. This gives green strength, and on heating leaves a residue with a good dry strength. Before the war it was nearly all imported. Some is produced in Britain, but, with restrictions in the manufacture of paper, the domestic output of sulphite lye has fallen correspondingly. Sulphite lye is also available as a solid which contains little water and so is more concentrated than the usual liquid form.

*Class 3.*

These are substances dissolved in a volatile solvent which evaporates on heating. For example, rubber latex may be dissolved in a solution of ammonia in water, and, on heating, the ammonia and water are driven off, leaving the rubber. The rubber may also be dissolved in a volatile organic solvent such as trichlorethylene, which again is driven off on heating. These rubber solutions, and subsequently the cores that they yield, give off unpleasant fumes on heating and are thus objectionable in the core shop.

Cellulose derivatives such as acetates and hydrates may be dissolved in organic solvents which evaporate on heating. All these cellulose solutions can be produced in Britain but are comparatively costly to manufacture.

*Class 4.*

These are oils which absorb oxygen on heating, leaving a solid residue of considerable strength and some elasticity. They are classed as drying, semi-drying or non-drying oils, according to the extent to which they absorb oxygen on heating. The value of this class of oil as a core binder may be roughly measured by the iodine value (I.V.). Linseed oil (I.V. about 190) is the most important drying oil and is used in a great variety of industries. Its green strength is low, but it gives very high dry strength. The drying of linseed oil on heating can be accelerated if it is previously boiled with driers such as manganese dioxide, but the dry strength of the subsequent core is somewhat reduced. During the preparation of linseed oil, by-products such as seconds, foots and linseed grease arise, which give progressively less dry strength and are also more variable in their properties. An alternative oil with a high dry strength is perilla (I.V. about 200). This is all imported and is not plentiful. Tung oil (I.V. about 170) dries very rapidly and produces a very high dry strength. It is, however, imported and comparatively expensive. Soya oil (I.V. about 130) is mostly imported, but during recent years the soya bean has been cultivated in Britain as a source of food. The oil is often hydrogenated and used as a foodstuff.

Corn oil (I.V. about 120) is a semi-drying oil produced from maize, and is largely used for food purposes. Cotton-seed oil (I.V. about 110) is a similar imported semi-drying oil, nowadays largely used in the manufacture of foodstuffs, such as butter and lard substitutes.

Some fish oils are in the drying or semi-drying class. Menhaden oil (I.V. about 150), from a fish resembling a large herring, is imported into Britain from the United States of America and used largely in the paint and varnish trades. Sardine oil (I.V. about 180), obtained from the waste material in the preparation of tinned



sardines, is often hydrogenated and used in the manufacture of soaps. Whale oil (I.V. about 140), formerly used extensively for quenching steels, is now largely hydrogenated for the manufacture of foodstuffs and soaps. Cod and seal oil (I.V. about 150) are also largely used as sources of foodstuffs.

#### *Class 5.*

These are colloids which swell with water and leave a hard residue on heating. Ordinary glue, for example, is obtained by heating animal matter such as skins and bones with water and steam under pressure. Glues are made in Britain and are used for a variety of purposes. A solution in water gives some green strength, and on evaporation leaves a residue with a fair dry strength. Fish glues, made from the heads, skin and bones of fish, have an unpleasant odour, are more hygroscopic than animal glues and develop less bond.

Casein, manufactured from whey remaining after milk has been used for making butter, is used to prepare casein glues. Casein dissolves in water containing a base such as borax, giving glue solutions stronger and more resistant to water than ordinary glues. Casein can also be obtained from the soya bean.

Albumin is a protein which is prepared from blood at abattoirs. It dissolves in water, especially if a base is present, giving a solution with little green strength. On heating, the albumin coagulates, giving a rather low dry strength.

Gum resins and gums are substances with somewhat similar properties and include ammoniacum, gamboge, myrrh, arabic, senegal and tragacanth. They emulsify with water, giving some green strength, and on heating leave a dry, often brittle, residue with a moderate strength.

#### *Class 6.*

This important group covers starches and their derivatives. Starch occurs in the seeds of cereals such as maize, rice and corn, leguminous seeds such as peas, beans and runners, and tubers such as potatoes, cassava (tapioca) and arrowroot. Flour is the finely ground meal of wheat or other grain, or of some tuber such as potato. Wheat flour, in addition to starch, contains gluten, which has appreciable adhesive properties in both the green and dried states.

On boiling with water, starches or wheat flour give starch or flour pastes with some green and dry strength. On heating or roasting, starches give gums, known as starch gums, which have better adhesive properties than the pastes. On heating with a small amount of mineral acid or alkali, starches hydrolyse to give dextrins, which are white or yellow powders, giving in core mixtures high green strength and considerable dry strength. Dextrins are the



best of the commonly used materials for providing green strength, though their dry strength is much inferior to that of linseed oil.

#### *Class 7.*

This covers binders of the sodium silicate type. Sodium silicates are made by fusing a mixture of silica sand and soda ash. The green strength of a water solution of sodium silicate is low, but the dry strength is moderately high, the change being due to the loss of water on heating. Binders utilising sodium silicate as a base have been successfully used in some foundries, both in Britain and on the Continent, but the refractoriness of the residue is only moderately high. The properties of sodium silicates as binders vary considerably with the ratio of silica to soda in their composition.

#### *Class 8.*

As mentioned above, cores can be made in sand mixtures containing clay as the binding material, without any organic binder at all. Such mixtures retain a considerable proportion of their strength during casting and also subsequently on cooling. Whether this is an advantage or a disadvantage depends on the circumstances in each particular case. Sometimes core-sand mixtures are used in which both clays and organic binders are present, and examples of this nature are described below.

#### *Properties and Use of Core Compounds.*

Core compounds are prepared by their manufacturers principally as core oils, core creams and semi-solid compounds containing dextrin and linseed oil as the most important constituents, with selected proportions of molasses, sulphite lye, resin or other binders, and some water. The properties of a core compound are the aggregate of those of its constituents, except for any modification that one constituent may produce in another. Dextrin gives high green strength and a fairly high dry strength, whilst linseed oil gives very little green strength but very high dry strength, so that, by altering the proportions of these, core compounds may be made with different properties as desired. Resin is waterproof and increases the water-resistant property of mixtures to which it is added. The optimum drying temperature varies for each material, so that the drying temperature chosen must be a compromise which will give the best all-round result.

The green and dry strengths are not the only properties of core compounds which are important. It is very desirable that the sand on the core bench should not dry off rapidly. Other factors are ease of working, flowability, resistance to water or water vapour, the nature of the core surface, the nature of the residue left after burning off and the amount and nature of the gases evolved during drying and during casting.

The amount of gas evolved on heating a core is of practical importance in the foundry, since if it is excessive it may lead to blows in the casting. The volume of gas evolved when a given core-binding material is heated can be determined by using the apparatus illustrated in Fig. 13. The core-binding material to be

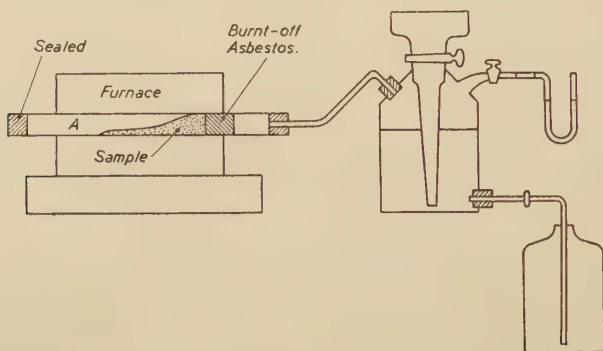


FIG. 13.—Apparatus for Determining the Amount of Gas Evolved from Core Sands.

tested is mixed in definite proportions with silica sand and baked at  $205^{\circ}\text{C}$ . A 50-g. sample of the mixture after baking is placed in the electrically heated silica tube *A* against a plug of burnt-off asbestos. The tube is heated to  $1000^{\circ}\text{C}$ ., and the gas evolved is collected over brine, the evolution of gas being complete when the pressure inside the apparatus becomes steady. A blank determination is carried out on the silica sand used, which is heated alone.

The amount of gas evolved can also be determined by heating to  $1000^{\circ}\text{C}$ . for 1 hr. a standard weight of 40 g. of the baked mixture already referred to. This is weighed after cooling, and the percentage loss in weight calculated. The results of examination for different classes of core-binding material are shown in Fig. 14. It will be observed that the bonding materials can be classified into groups with regard to the quantity of gas evolved, as follows :

- (a) Thin oils.
- (b) "Compounds" (*i.e.*, mixtures of organic substances with saponifiable oils).
- (c) Organic solids.
- (d) Water-soluble liquids.
- (e) Clays.
- (f) Sands.

Each class of material gives a group of results which is distinct from the others and characteristic of its class. There is a relation between the loss in weight and the gas evolution for each class of material, so that either method of investigation may be adopted. That is,

if a loss-in-weight experiment is carried out for a given material, the volume of gas evolved may be obtained from the graph with a

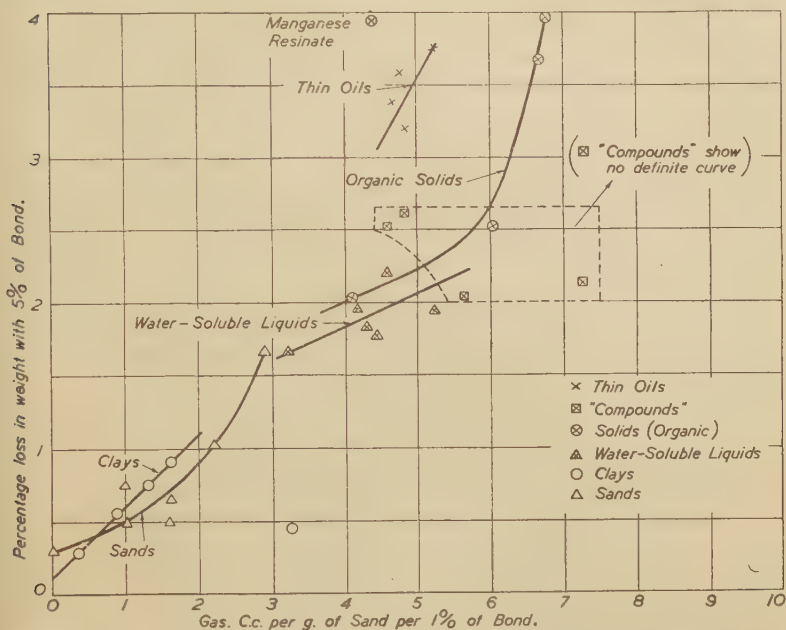


FIG. 14.—Relationship between Gas Evolution and Loss in Weight for Various Types of Core Bond.

sufficient degree of accuracy. This does not apply to the so-called core "compounds," and for such materials the loss in weight is not a reliable guide to the quantity of gas evolved on heating.

#### Means of Reducing the Consumption of Core Compounds.

The methods by which the consumption of core binding materials per ton of castings can be reduced may be roughly classified as follows :

- (1) Replacement of core sands by green sand or dry sand.
- (2) Ensuring that core compounds and binders are used correctly and without waste.
- (3) Reduction in percentage of binders in core-sand mixtures.
- (4) Addition of a silica flour or clay to core-sand mixtures.
- (5) Utilisation of alternative materials, including available waste products.

These methods are referred to in greater detail below, and some examples are given which, it is hoped, will suggest how the

consumption of core binders may be reduced in any particular foundry, the course to be adopted naturally varying with local conditions and equipment.

Where small green-sand castings are being manufactured, green-sand cores can in many cases be used instead of oil-sand cores. These green-sand cores collapse after the pouring of the casting almost as well as oil-sand cores, but their application is somewhat limited. In general, the shape of the core must be such that it is well supported in the mould, so that it does not sag. Where there is much overhang, whole green-sand cores cannot be used much, since their mechanical strength is low. Frequently, however, this difficulty can be overcome by turning out green-sand top halves on to dry-sand bottom half cores. Where moulding is done on the floor, or in a pit, much larger green-sand cores can be used, since they can be built up on the spot and do not have to be transportable. Large green-sand cores must be simple in shape; they have frequently been used, for example, in the casting of open-hearth charging boxes.

In many instances, oil-sand cores are used where there is no real necessity to have a collapsible core. In such cases dry-sand cores are frequently strong enough and give good results in practice. Sometimes in green-sand working, inserts of oil-sand are put in front of the runner, or in other places, to minimise erosion during pouring. Runner bushes and similar articles are sometimes made in oil-sand mixtures to provide a standby job in the core shop and to be held in stock. In many cases dry sand can be used equally well for such purposes, but dry-sand parts cannot, of course, be kept in stock.

When core sands are being mixed, both the silica sand and the core compounds or the core binders should be measured as accurately as possible in order to avoid waste. The silica sand may be measured in buckets- or skips-full. Core oils and core creams can be measured by volume, whilst semi-solid compounds are best weighed out. Similarly, linseed oil can be added in pints and dextrin in pounds weight. Water should be added in pints. The silica sand should be cold. If insufficient time is allowed, hot sand may come either from the sand drier, or, if a proportion of reclaimed sand is being used, from the knock-out heap. The milling of warm mixtures encourages drying-off on the core bench. The wastage of core-sand mixtures due to drying-off, some of which is inevitable, occurs with greater readiness as the percentage of dextrin is increased. It may be reduced by the addition of molasses, or by using water in the mixture containing a hygroscopic salt in solution, such as ammonium nitrate, or by covering the heaps of sand on the core benches with wet cloths or sacks. Baking of the cores at the correct temperature is necessary for the maximum strength to be obtained from the core binders used, the dry strength of both under-baked and over-baked cores being less than that of

correctly baked cores. The time of baking can be minimised by ensuring an adequate number of air changes.

In foundries it is easily possible for unnecessarily large percentages of core-binding materials to be used. Often the same core-sand mixture is used for cores of widely different sizes, shapes and weights. The strength of the mixture is made ample for the most exacting cores, and is far greater than is necessary for some small light cores. Sometimes this is due to the small capacity of the mixing equipment, but more often it is due to the fear that confusion may arise if two or three different mixtures are present in the core shop at the same time. Sometimes cores are purposely made very strong to allow for rough handling, but this, in any case, should be avoided. In some instances cores with overhanging parts are made sufficiently strong to be self-supporting, whereas a shaped support would enable a less strong core to be handled safely.

In some foundries core-sand mixtures containing proportions of 4%, 5% or even more of organic binders are regularly used for all types of core. Table XXIII. gives the results of examining mixtures

TABLE XXIII.—*Chelford Silica Sand with G.B. Kordek and Linseed Oil.*

A.F.A. test cylinders 2 in. × 2 in.  
Samples baked at 200° C. for 2 hr.

Mixture.	Permeability No.	Water. %.	Green Strength, Lb. per sq. in.	Dry Strength, Lb. per sq. in.
1500 g. Chelford sand . 17½ g. G.B. Kordek . 10 c.c. Linseed oil .	94	2.5	1.9	1060
1500 g. Chelford sand . 15 g. G.B. Kordek . 10 c.c. Linseed oil .	111	2.7	1.35	1040
1500 g. Chelford sand . 10 g. G.B. Kordek . 10 cc. Linseed oil .	120	2.6	0.95	610

of Chelford silica sand with smaller amounts of G.B. Kordek and linseed oil, the total percentage of binders being 1.8, 1.67 and 1.25%. Even with only 1.25% of binders the mixture works well; in fact, small cores were successfully made in it and gave satisfactory results on casting. In this case the green strength is inadequate for making large cores or cores with any overhang. In Table XXIV. are given the results obtained from Chelford sand mixtures containing 2.7, 2 and 1.7% of a proprietary core compound. All these mixtures have been found perfectly satisfactory for making medium and large cores.

In some cases cores of unusual shape call for mixtures with high green strength. This may be secured by the addition to the



TABLE XXIV.—*Chelford Silica Sand with Kordol No. 3.*

A.F.A. test cylinders 2 in. × 2 in.  
Samples baked at 200° C. for 2 hr.

Mixture.	Permeability No.	Water. %.	Green Strength, Lb. per sq. in.	Dry Strength, Lb. per sq. in.
1500 g. Chelford sand .	91	4.2	1.9	1600 unbroken
40 g. Kordol No. 3 .				
1500 g. Chelford sand .	112	3.0	1.8	1500
30 g. Kordol No. 3 .				
1500 g. Chelford sand .	120	3.0	1.25	910
25 g. Kordol No. 3 .				

mixture of either silica flour or a clay, instead of by using an excessive amount of core compound. Silica flour will not interfere with the collapsibility of the core after casting, whereas added clay will retain much of its bonding strength after the casting is poured. In both cases, although the green strength is increased, the dry strength is reduced, and this imposes a practical limit on the amount of silica flour or clay which can be used. The presence of these fine materials in the mixture makes the sand less easy to work on the core bench, diminishes the plasticity of the sand mixture and also lowers the permeability of the sand. Table XXV. illustrates the effect of

TABLE XXV.—*Chelford Silica Sand with Silica Flour and Linseed Oil.*

A.F.A. test cylinders 2 in. × 2 in.  
Samples baked at 200° C. for 2 hr.

Mixture.	Permeability No.	Water. %.	Green Strength, Lb. per sq. in.	Dry Strength, Lb. per sq. in.
1500 g. Chelford sand .	68	6.7	0.9	400
150 g. Silica flour .				
15 c.c. Linseed oil .				
1275 g. Chelford sand .	53	6.6	1.25	420
225 g. Silica Flour .				
15 c.c. Linseed oil .				
1200 g. Chelford sand .	42	6.7	2.1	400
300 g. Silica flour .				
15 c.c. Linseed oil .				

adding silica flour to a mixture of Chelford silica sand and linseed oil. As the proportion of silica flour increases the green strength increases with no significant change in the dry strength, the permeability being diminished at the same time.

Other mixtures containing clays as well as core binders gave the

results shown in Table XXVI. The first mixture included old green sand which contained about 5% of Fulbond No. 1, and the results

TABLE XXVI.—*Silica Sands with Core Binders and Clay.*

A.F.A. test cylinders 2 in. × 2 in.

Samples baked at 200° C. for 2 hr.

No.	Mixture.	Permeability No.	Water. %.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
	Proportions.				
1	1000 g. Chelford sand				
	500 g. Old green sand	87	3.5	4.8	680
	40 g. Kordol No. 3 .	75	5.2	4.1	500
2	1000 g. Chelford sand				
	500 g. Old green sand	108	2.5	3.25	430
	20 g. Truline .				
	20 g. Sulphite lye .				
3	1500 g. Chelford sand				
	10 g. Fulbond No. 1	73	3.75	3.2	510
	45 g. Truline .				
	15 g. Sulphite lye .				
4	1000 g. Chelford sand				
	750 g. Kings Langley red sand .	94	5.2	5.2	530
	15 g. G.B. Kordek .	94	5.7	3.8	630
	15 g. Truline .				
5	1200 g. Leighton Buz- zard No. 9 .				
	300 g. Kaybond .	82	5.1	4.0	750
	30 c.c. Linseed oil .				
6	1200 g. Chelford sand				
	300 g. Kaybond .	26	6.7	3.8	680
	30 c.c. Linseed oil .				

may be compared with those of a similar mixture without any clay shown in Table XXIII. With the clay mixture the green strength is increased and the dry strength reduced very considerably. There is here no reduction in core binder but a readjustment of green and dry strength. In the second mixture the Kordol was replaced by Truline and sulphite lye, giving somewhat lower green and dry strength, and the mixture proved rather sticky in the core shop. In the third mixture a direct addition of Fulbond No. 1 was made and the proportions of Truline and sulphite lye were varied; this mixture was made into small cores which proved satisfactory, although care was necessary in withdrawing the cores, as they were inclined to adhere to the core box. The fourth mixture contained clay only in the form of a thin film round the grains of the King's Lynn red silica sand. It was used successfully in making cores for a steel casting weighing about 1 ton.

It will be noticed that mixtures 2, 3 and 4 contained the resin Truline in place of linseed oil. It was found that in baking the

mixtures some of this resin was liable to volatilise, leaving a weaker surface. This tendency may be avoided by applying part of the resin dissolved in a volatile organic solvent as a coating, which for small cores may be sprayed on before stoving and for heavy cores brushed on after stoving. In mixtures containing silica sand with no added clay or reclaimed sand, better results can be obtained if the linseed oil is not omitted entirely but is replaced in part by

TABLE XXVII.—*Experiments with D.C.L. Slop.*A.F.A. test cylinders 2 in.  $\times$  2 in.

Samples baked at 200° C. for 2 hr.

Mixture.		Permeability No.	Water. %.	Green Strength. Lb. per sq. in.	Dry Strength. Lb. per sq. in.
No.	Weights. G.				
1	1470 Chelford sand . 30 Slop .	144	0.6	0.9	180
2	1455 Chelford sand . 45 Slop .	132	0.9	0.6	630
3	1455 Chelford sand . 45 Slop . 10 Dextrin . 5 Fulbond No. 1 .	150	0.9	1.8	600
4	1455 Chelford sand . 45 Slop . 10 Dextrin . 5 Fulbond No. 1 . 10 Linseed oil .	143	0.9	1.9	860
5	1455 Chelford sand . 45 Slop . 10 Linseed oil . 5 Fulbond No. 1 .	137	0.9	1.1	1010
6	1455 Chelford sand . 45 Slop . 5 Dextrin . 5 Fulbond No. 1 . 10 Linseed oil .	137	0.9	1.8	1020
7	1455 Chelford sand . 45 Slop . 10 Dextrin . 10 Linseed oil . 15 Fulbond No. 1 .	162	0.9	3.6	740
8	1425 Chelford sand . 45 Slop . 30 Fulbond No. 1 .	158	1.8	2.4	90
9	1305 Chelford sand . 45 Slop . 150 Kaybond .	100	2.1	1.2	130
10	1500 Chelford sand . 15 Slop . 15 G.B. Kordek . 6 Linseed oil .	120	2.0	1.6	550
11	1500 Chelford sand . 15 G.B. Kordek . 15 Slop .	150	1.5	1.6	160

using resin dissolved in linseed oil. In mixture 5 the base sand was Leighton Buzzard No. 9, which is coarse in grain size, whilst No. 6 contained Chelford sand, the grains of which are of medium size. The effect is seen in the permeability number, which, at the moisture used, is very low in the case of the Chelford mixture. Both these mixtures had high green strength with dry strength adequate for small cores, but they were somewhat lacking in plasticity. The clay used, Kaybond, is much more refractory than the Fulbonds but less efficient as a clay binder.

The Members of the Sub-Committee have carried out experiments with several industrial waste and by-products in endeavours to find materials of value as core binders, and the results of one such investigation are shown in Table XXVII. The material, D.C.L. Slop, is a viscous liquid resembling molasses in appearance. The first seven mixtures incorporate various proportions of dextrin, Fulbond No. 1 and linseed oil, using Slop as the main binder. Mixtures 8 and 9 contain only Slop as organic binder, with additions of Fulbond No. 1 and Kaybond, respectively. The dry strength of these was inadequate, both mixtures giving weak friable cores. Mixtures 10 and 11 are alike except for the presence of linseed oil in No. 10. The absence of this oil in No. 11 is responsible for the much lower dry strength.

Mixture No. 4 appeared promising from a practical point of view. On trial it worked easily in the core shop, did not air-harden and gave hard cores after baking. Cores were successfully made in it and used in a number of castings. Mixtures 5 and 6 were somewhat similar in constitution and also behaved quite well. The linseed oil present, apart from increasing the dry strength, also improved the ease of stripping from the core box.

By-product materials of this type can be utilised as foundry binders in two different ways. Where foundries make up their own mixtures from core-binding materials, the by-product can be added as a constituent of the mixture. Alternatively, the by-product can be used by manufacturers of core compounds in making up core creams or semi-solid compounds. This is probably the more economic method of utilisation, since the mixing and blending of core-binding materials can be carried out more efficiently by the core-compound manufacturers than by most foundries.

### *Conclusion and Recommendations.*

In view of the shortage of materials ordinarily used for making core compounds, core sands consisting of silica sand and organic binders should not be used except when really necessary. Foundries using ready-made core compounds are recommended to try core-sand mixtures containing smaller proportions of core compounds than they have normally used. The arrangements for handling cores, both before and after baking, can frequently be improved

without much difficulty, and the need for excessive strength in cores thus reduced. Core creams should be used instead of semi-solid compounds wherever possible. Foundries making up their core sands from dextrin, linseed oil and other core materials should also carry out experiments using reduced proportions of these materials, aiming especially at decreasing the proportion of dextrin in the mixtures.

Where cores are made in the same shop in a variety of sizes and shapes, they should be classified according to the green and dry strengths required, and different core compounds used for each class, small or simple-shaped cores naturally requiring a smaller proportion of core compound than others. To obtain the most economical results from organic binders, it is essential to weigh or measure out both the sand and the binder and to mill the mix thoroughly. To avoid waste, core sands should not be allowed to dry off on the bench; the easiest way to avoid this is to keep them covered up.



*DISCUSSION.*

Mr. W. J. DAWSON (Chairman of the Steel Castings Research Committee; Messrs. Hadfield's, Ltd.) Sheffield: I should like to pay my tribute to the work of Dr. Rees as Chairman of this Sub-Committee and his collaborators. Dr. Rees is a veteran in the examination of sands; he was carrying out such work about the period of the last war. The degree of accuracy to which the testing of sands has now been developed is noteworthy and the Members of the Sub-Committee have contributed in no small measure to this.

If one looks at some of the results, for example, those set out on p. 409 P of the Report, where parallel tests on the same samples were carried out in foundry laboratories and in the Refractories Department of the University of Sheffield, the reliability of the method is evident, the results agreeing quite as well as could be expected in such a series of tests.

A further feature to which I would direct attention is the very interesting curves in Fig. 6, which illustrate so clearly the marked difference in the drying time between two different moulding materials containing exactly the same moisture content.

The results on the insulating sands are of great interest. Sands of this type have important possibilities in the foundry, enabling advantage to be taken of the principle of differential cooling as applied in the steel plant for the production of sound ingots. In particular, these insulating sands should prove efficacious in the preparation of so-called "blind feeder-heads," which are coming into use and for which purpose insulating sands may be employed to economise in the size of the feeder-head.

The Sub-Committee in this Report have put at the disposal of foundrymen most valuable data, which are already being put to practical use.

Mr. N. D. RIDSDALE (Messrs. Ridsdale & Co., Ltd., Harrogate): I should like to deal first with chemical analysis, and ask the Sub-Committee how much use they think that ordinary chemical analysis of the sand, as a whole, really is, and whether they would consider that if they separated the clay grade from the quartz grade and analysed both grades separately, or at any rate the clay grade, the information so derived would be very much more useful. Again, I would inquire whether in the sieving tests mentioned in the Report, the clay grade was separated by washing before the tests were made, or not. I presume that it was, because, in my opinion, the tests would not be of much use unless the clay grade was first separated by washing and the sieving done on the quartz grades.

Turning to pp. 415 P-416 P dealing with the B.C.I.R.A. air-permeability apparatus, there is no doubt that if the policy is followed of weighting the sliding bell more and more as the permea-

bility of the sand increases, in order to try to maintain a constant manometer pressure of 10 cm. of water, friction will interfere with accurate readings on sands of high permeability; but surely the best procedure is to test such sands at a reduced pressure of, say, 5 cm. of water—or even less if the bell is light enough—thereby increasing the time of descent of the bell sufficiently to minimise, if not eliminate, the effect of friction.

In view of these experiences with the B.C.I.R.A. apparatus, a number of people who are using the Dietert modification of the A.F.A. permeability meter may be asking themselves how that apparatus might behave as regards friction when dealing with sands of high permeability and when using this "time-pressure" method, which is the method used by the Sub-Committee. In the short time at my disposal since receiving this Report the best that I could do was to time the descent of the sliding bell of the Dietert apparatus when the pipe leading from the air-chamber to the test-piece was open and no test-piece was inserted. Under those conditions 2 litres of air escaped from the reservoir in 2 sec. compared with 2 litres in 10 sec. as mentioned at the foot of p. 415 P for the B.C.I.R.A. apparatus. That is a good indication that the American-designed permeability apparatus is relatively free from friction troubles.

I should like to draw the attention of the Sub-Committee to the permeability method which is almost universally used in America and is known as the "orifice-plate" method. In that method it is necessary only to measure the pressure and not the time; the bell is descending very slowly, and friction is reduced to a minimum on that account. This orifice-plate method was, I think, first proposed by C. M. Saeger of the U.S. Bureau of Standards. I have no doubt that the Sub-Committee know of its existence, but they may say that it is not sufficiently accurate. My experience of it, after making a number of comparisons, is that, though it is only approximately accurate to within about 10% when using the dial which is on the Dietert permeability meter, if the height of the manometer water column is accurately measured and a table be consulted, the readings obtained in that way are quite sufficiently accurate for all ordinary purposes and cover a very wide permeability range—I think the range is from almost zero to about 1,000 permeability number.

The orifices could be fitted to the B.C.I.R.A. air-permeability apparatus, but in this case it would be better to eliminate the test-piece holder shown in Fig. 7 of the Report and substitute a trough with a mercury seal into which a test-piece holder consisting of a plain 2-in. dia. tube could be inserted. Talking about permeability number, in the data given in the Report from p. 398 P onwards, I presume that the Sub-Committee refer to what I would call the American Foundrymen's Association permeability number. The B.C.I.R.A. in its Research Report No. 108 (1934), pp. 46-48, recorded some tests of sands, including permeability numbers. The average foundryman, unless he is aware of the fact that the A.F.A. and the

B.C.I.R.A. permeability numbers are not strictly comparable, may be misled by the figures, and I suggest that in these pages of the Report it should be made clear that it is the A.F.A. permeability numbers which are used—if that is the case—and not the B.C.I.R.A.

Mr. R. C. TUCKER (Messrs. Newton Chambers & Co., Ltd., Sheffield) : I have read the Report with very great interest. Through the manufacture of 30% chromium cast iron my firm has had experience which approaches steel-foundry practice as well as our normal cast iron production, and because of this I wish to stress certain aspects of the Report in order that cast iron foundrymen will not be led astray :

(a) The sands used are very open indeed, and because of this several factors come into play.

(b) The steel moulder rams his green-sand mould much harder than an iron moulder would.

Hence the idea of increasing the A.F.A. test from three to ten blows, but still the sand remains very open indeed. Hence also the modification to the B.C.I.R.A. permeability holder.

An improved method of reporting A.F.A. results, adopted in our laboratories, is to include the weight of sand used and a little diagram showing the location of the distance mark between the plus and minus limits, *e.g.*, 170 g.  $\pm$  —. This would give the average density of ramming, and after ten blows this density should be uniform.

Inclusion of these figures would enable those who use the “ scientific ” B.C.I.R.A. ramming-density method of preparing test-pieces to make a correlation.

Cast iron moulders, on the other hand, use sands which are not so open, because of the better fluidity or ease of penetration of cast iron. Hence, they must not and do not ram so hard, and the A.F.A. test is designed to approximate to an average green-sand ram. Actually, even with three blows, the ramming tends to exceed that necessary for most green-sand moulds. Very few cast iron sands indeed are open enough to give rise to the difficulty encountered in measuring permeability. The modification introduced is, however, timely and should be adopted by all foundries. Incidentally, we shall use it for testing oil-sand cores, as well as green-sand.

The argument concerning the mass of air varying with the pressure brings one to the cross-roads always encountered in sand testing. Are the tests to be purely scientific and to consider scientific aspects exclusively, or shall the test reproduce as faithfully as possible the manufacture of a mould? The A.F.A. test belongs to the second category, and to split hairs about “ masses ” of air at slightly different pressures is in itself not scientific. In an open sand the pressure is lower both in the test (B.C.I.R.A. pattern A.F.A. permeability tester) and in the mould. If one must have scientific sand testing, the B.C.I.R.A. or the modified A.F.A. (double com-

pression, 4-in.  $\times$  2-in. dia. cores, rammed to a definite density or "index of ramming") methods offer better possibilities.

Finally, the use of the Dietert hardness tester enables one to correlate the A.F.A. three-blow test with mould hardness in the foundry. I carried out a test this morning on a synthetic sand which contains a high proportion of used synthetic sand (a point where the Sub-Committee are at a disadvantage in investigating new sands), with the following results :

Dietert hardness :	3 Blows.		
	Test A.	Test B.	10 Blows.
Top . . . . .	90-90	86-91	95-95
Bottom . . . . .	84-84	80-81	90-90
Foundry mould hardness :			
Normal . . . . .	60-70		
Too hard (above normal; scabs will form) .	90		
Too soft (below normal; swells and drops) .	20		

This shows that the ten blows are unsuitable for some sands and for cast iron work, as was indicated previously.

Mr. J. BLAKISTON (Modern Foundries, Ltd., Halifax) : I congratulate the Sub-Committee on their excellent effort on a difficult and complicated subject. Bentonite is a good servant though a bad master, and it has always to be treated with respect. The substitutes for it may be very satisfactory, but they have to be treated with even more respect. One can carry on with them very smoothly, producing satisfactory castings, and then one day the sword of Damocles falls, filling the foundry with defective castings during its descent.

Great Britain suffers from an excessive variety of moulding sands ; there are sands available for every operation that takes place in the foundry—so many that the founder does not know which to choose, and the Sub-Committee are doing good work in tabulating the various properties and sources of sands. At the present moment there is a great overlapping of transport, sand from the north being taken to the south and *visa-versa*, causing great wastage of transport.

On checking through the Report I disagree with the statement on p. 395 P that too much stress is placed upon the importance of high permeability in cores ; incidentally this statement is contradicted in the portion on top of p. 446 P. It is my experience, which covers all types of intricate cored castings, that half the time of the metallurgist is wasted by attributing defects to a metallurgical cause when it is the permeability of the core that is at fault.

Further down p. 395 P I note that special attention is directed to the desirability of the calibration of pressure gauges on hydraulic machines for the measurement of dry strength. I have used the Hounsfield tensometer miniature testing machine, fitted with a compression device, for this purpose. This machine is accurately



calibrated up to 2 tons. Not only are the results easily read, but they are transferred to a graph. I think this apparatus is worthy of consideration by the Sub-Committee.

I agree with the last speaker in the discussion when he questioned the number of blows of the standard rammer for the various tests. When this rammer was evolved a number of iron moulders rammed several moulds simultaneously; the average density of the moulds was transferred back and found to equal three blows. The steel moulder, however, has to ram much harder to achieve a satisfactory casting, and I think that when testing steel moulding sands a larger number of blows should be taken as standard.

With reference to p. 415 P, we are all aware that the existing foundry permeability apparatus has its drawbacks, but nevertheless it has been installed in most foundries, as it can be worked accurately by untrained personnel and the readings are required only for comparative purpose. The introduction of new methods of measuring permeability would only lead to confusion.

I am disappointed that the Sub-Committee have not seen fit to carry out their investigations further on the expansion of sand mixtures containing clay (p. 419 P). I am convinced that a number of casting defects are caused by the thermal expansion of moulding sands.

The apparatus for the determination of the amount of gas evolved from core sands, Fig. 13, is becoming increasingly important in view of the dilution that is taking place in core compounds. I have had some bitter experiences caused by this dilution, as many diluants, some of which have been suggested in this Report, precipitate heavy carbon deposits in the form of soot in the mould during the casting operation; this carbon is either absorbed by the metal, giving an incorrect analysis, or is trapped in the casting, creating visible defects.

The SECRETARY (Mr. K. Headlam-Morley) : With regard to what Mr. Blakiston has just said I should like to state that the Foundry Bonding Materials Control is giving attention to this matter of cross-traffic of sands. We hope that compulsion will not be needed, and we are confident that we shall get the wholehearted co-operation of the industry in putting the use of our own sands on the most economic basis and reducing transport.

Lieut. P. J. Boor (The Hercules Powder Co., Inc., Wilmington, Delaware, U.S.A.) : I wish to congratulate the Sub-Committee on their Second Report, which brings forward many valuable suggestions on the limitation of the use and substitution of core-binding agents, vitally needed for other aspects of the war effort.

As I have had some experience in the use of resinous core-binders such as Truline, I should like to make some remarks in this connection.



I have found it confirmed that in many instances up to a 50% replacement of linseed oil by Truline gives equal, and, I may add, in some cases, better, results. In other instances I found that Truline binder can be used to advantage without any oils, particularly in such cases where reclaimed or return sands are used, as Truline is not absorbed by the fines in such sands. With increased interest in the use of return sands, this seems to me a point of considerable importance.

In general I have found that Truline renders possible a reduction of the baking time and that the results may even improve in consequence. Thus, better strength figures may be obtained, while a larger output of cores per day is made possible.

The suggestion is made in the Report that it may be desirable in some cases to dissolve resins in linseed oil before addition to the sand. I would mention that Truline can be added before and separate from linseed oil, thus leading to more complete control of the proportions of each binding agent. In my view, in a large number of foundries facilities are not available to effect complete solution of the resin in linseed oil.

In regard to the use of Truline in combination with sulphite lye, where quick drying of the core surface is experienced, I may suggest that the restoration of moisture to the core surface before baking by spraying or brushing with water represents a simple expedient to deal with some cases of that nature.

Finally, a less well-known use for Truline in Britain is its incorporation in green-mould facing sand. Here it replaces cereal binder, where used for this purpose, and in the United States Truline finds wide application in this way.

This replacement is reported to result in better flowability of the sand and on air-drying it develops a high compression strength and mould hardness.

Dr. J. G. A. SKERL (Sternol, Ltd., London): I wish to draw attention to pp. 446 P and 447 P dealing with the amount of gas evolved on heating a baked core sand and the relation between the amount of gas and the loss of weight for various types of core bond. The information given in Fig. 14 may be very misleading for several reasons. It is stated that "the core-binding material to be tested is mixed in definite proportions with silica sand and baked at 205° C." Under practical conditions it is known that different proportions of binder have to be used to give the same result, depending on the type of binder, and that a temperature of 205° C. would not be suitable for most types. This temperature would destroy some binders, whilst it would be insufficient to dry out thoroughly core sands containing, in particular, the thin-oil type, with the result that more gas would necessarily be evolved on heating, either in a furnace (as illustrated in Fig. 13) or on casting metal in a mould. Any conclusions based on collecting gas

over brine or other aqueous solution is bound to be fallacious, as the products of combustion almost invariably contain water and other materials which will be condensed, as well as true insoluble gases.

The point must be emphasised that gas evolution is secondary to bonding efficiency, in the green and dried states, of core compounds under practical conditions, and that in general a higher percentage of sands, clays and water-soluble liquids would be used than "compounds" and thin oils. Hence, given proper and adequate technical control of mixing and drying in a foundry, there will be little difference in the total amount of gas evolution between cores made with varying materials of normal quality.

I wish to endorse everything that has been written about the need for economy in the use of core oils and compounds. They are almost entirely made from imported materials, and the war effort will be assisted if foundrymen learn to use them in the most efficient manner. I feel certain that I am speaking for the manufacturers of these materials in saying that we would welcome the opportunity of assisting the foundry industry in this matter.

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### CORRESPONDENCE.

Mr. W. M. LORD (The Sandholme Iron Co., Ltd., Todmorden, Lancs.) wrote: I have read with considerable interest Section IV. of the Second Moulding Materials Report dealing with core binders and their use. This subject has claimed my attention for some time past with a view to finding more efficient core binders than are at present in use.

Whilst the consideration of cheapness enters into the problem, it would appear that many synthetic products could be used as efficient binders, and I think that here is a field open for the organic chemist to collaborate with the foundry technologist in producing a really efficient synthetic product for sand binding.

At present none of the proprietary products on the market is entirely free from objection—all evolve gases in large or small quantities, which very often have an objectionable smell, irritating to the nose and throat. The strengths and other physical properties of the cores vary over a wide range.

The list of materials for sand binding which is mentioned in the Report is by no means complete and many additions can be made thereto, but it is realised that many products may not be obtainable at present.

Mention has been made of synthetic resins, but no reference to their most important properties of thermo-setting and thermo-hardening appears in the text. This latter property, as is shown by the Bakelite type of resin, seems to offer tremendous possibilities to foundries on quantity production work where the necessary metal

core-boxes are available; cores could be turned out in large quantities of extreme accuracy without the necessity for any stoving.

Other interesting synthetic or natural materials which would probably repay investigation are :

(1) Oiticica oil from Brazil, which is stated to have the highest iodine value of any known oil, *i.e.*, 231.

(2) Ethyl cellulose—a product insoluble in hot water but soluble in cold, yielding a stiff paste.

(3) Alkyl silicates which hydrolyse in the presence of water, yielding silica, which itself acts as a binder (British Patent No. 290,717). This patent mentions their use as sand binders.

Mr. C. H. KAIN (Messrs. Lake and Elliot, Ltd., Braintree) wrote : At present steel foundry interest is largely concentrated on synthetic green-sand moulding, and the work of the Sub-Committee on bonding materials will be most helpful. Reference is made on pp. 394 P and 428 P to the life of Fulbond. It will be interesting to know if any data have been collected upon the actual consumption of sand when using various bonding agents. My own experience is that a greater amount of new sand is necessary with Fulbond than when using Colbond or bentonite. I have no accurate data of other bonds.

We find that it is necessary to increase the consumption of new moulding sand by about 25% when using Fulbond as against bentonite. Thus, if the consumption in the foundry of moulding sand, as distinct from core sand, is 12 cwt. per ton of castings produced when bonding with bentonite, it will be necessary to increase this consumption to 15 cwt. per ton when using Fulbond. If this increased amount of new sand is not used, the quality of the castings (in smaller sizes) rapidly deteriorates.

I think the Sub-Committee underestimate the efficiency of Fulbond when compared with the efficiency of bentonite. The following data show that the efficiency of Fulbond as a bond is approximately equal to that of bentonite :

	Moisture, %.	Strength, Lb. per sq. in.	Permeability No.
Arnolds 19 sand + 0.74% core gum plus—			
2.2% Fulbond No. 1 . . . . .	3.0	6.85	447
	3.0	8.45	505
2.2% Fulbond No. 3 . . . . .	2.5	7.0	458
	2.25	6.20	482
2.2% Bentonite . . . . .	2.5	6.20	498
	2.75	7.15	463

Milling time, 4 min.

I think that the fusion point of Fulbond is overestimated at 1290° C.; even at this temperature it is over 100° C. less than that of bentonite and over 200° C. less than that of Colbond.

In using Fulbond in the iron foundry no extra addition of new

sand is necessary. We have in Braintree a continuous iron foundry system, which has been running now for several months, with no addition of new sand other than a little burnt sand falling out of the cores. The only additions are Fulbond and coal-dust.

### SUB-COMMITTEE'S REPLY.

In replying to the discussion the SUB-COMMITTEE first desire to thank the contributors to it for their appreciative remarks and for their constructive suggestions.

Mr. Ridsdale's comments with regard to the comparative values of chemical analysis of the moulding sand as a whole and of the separated clay grade are of interest; the former undoubtedly has its value, especially with the strong finer-grain moulding sands which are diluted as required with coarser high-silica sands, in forecasting the likely behaviour of the sand in contact with hot metal. It is essential to be guarded in making deductions from chemical analyses of the clay grades, as in nearly all the naturally-bonded sands examined the clay grade contains varying proportions of silica of "clay-grade" dimensions. A comprehensive mineralogical analysis is likely to be of more use than the chemical analysis, and the relationship between the mineralogical composition and the behaviour of moulding sands both in laboratory tests and in iron and steel foundry service is being examined by the Sub-Committee. In most cases the sieving tests of the moulding sands referred to in Section II. were made on the sand grades following removal of the "clay" by washing, but in the case of the bonded sandstones from County Durham discordant results were obtained when this was done and the gradings given are on the milled sandstones as prepared for foundry use. Chemical analyses were made of the "clay grade" in some cases and these gave the following results:

	Raynham Estate.	I.M. Sand.	Higher Kinnerton Sand.	Alderley Edge Sand.	Dead Friars Quarry Milled Stone.
Silica. % . . .	71.67	65.87	68.46	71.40	67.36
Alumina. % . . .	14.64	18.21	16.62	15.86	16.95
Iron oxide. % . . .	5.26	5.46	3.85	2.26	2.54
Titanium oxide. % . . .	0.48	0.51	0.31	0.51	0.62
Lime. % . . .	1.21	0.55	0.35	0.64	0.61
Magnesia. % . . .	0.21	0.42	0.61	0.71	0.95
Alkalis (as K <sub>2</sub> O). % . . .	1.35	1.62	2.86	2.74	2.64
Loss on ignition. % . . .	5.08	7.24	6.86	5.92	8.21
Total. % . . .	99.90	99.88	99.92	100.04	99.88

Microscopical examination showed that all these "clay grades" contained a good deal of finely divided quartz.

It should be pointed out that the refractoriness and sintering



tests collate with foundry tests, especially in regard to "burning-on" tendency; the hot-strength of moulding sands is being investigated by the Sub-Committee, and these tests are yielding useful information with regard to both burning-on, &c., and collapsibility. It is indicated in the Report that A.F.A. test-pieces were used in examining the moulding properties, and the permeability numbers given are therefore A.F.A. numbers.

It is the opinion of the Sub-Committee that the basis of the testing of moulding sands, both naturally-bonded and synthetic, should be as accurate as it is possible to make it, and the apparatus used should be such as will eliminate the personal factor of individual operators. Mr. Tucker refers to the variable ramming densities used in foundry practice, and in order to provide information covering the general range of ramming densities the tests are now being made with 3 and 10 rams, and in some cases 15 rams, in the A.F.A. type machine. With most sands in the as-used condition the rate of increase in density beyond 10 rams is very small. The Dietert hardness tester referred to is unquestionably a useful tool in both the laboratory and the foundry, and further reference to mould hardness tests will be made in a subsequent Report.

Although the Sub-Committee consider that the small differences in the thermal expansion of the moulding sands examined for this property are unlikely to have any significant effect on the behaviour of the sands in casting, it is evident from Mr. Blakiston's contribution to the discussion that the range of sands examined must be widened, and this is being done. The results obtained will be collated with the behaviour of the sands in practice. Mr. Blakiston's reference to the use of the Hounsfield tensometer miniature testing machine is most useful, and, as tests which have now been made fully confirm the comment on it, it is hoped to use it in future dry-strength tests.

The remarks on pp. 395 P and 446 P relating to the permeability of cores are not contradictory, but when read in conjunction with their contexts are quite compatible. Further, the statement on p. 446 P refers to excessive gas evolution from a core, whereas that on p. 395 P refers to the bearing of permeability on the economy of bonding material—in effect, a consideration of two entirely different aspects of the problem.

Lieut. Boot's comments on the possibilities of Truline binders are timely and will doubtless receive attention from foundrymen. The Sub-Committee agree that in many core mixtures up to 50% of the linseed oil may be replaced by Truline, provided that the stove temperature and the baking time are closely controlled.

The Sub-Committee are especially indebted to Mr. Lord for his comments on core binders and the possibilities of synthetic resins and other materials for this purpose, and they look forward to collaboration with Mr. Lord in a comprehensive examination of materials which are, or may be, commercially available. The



results of a series of laboratory tests on alginates as a core-binder are already under consideration.

Mr. Kain's references to the efficiency of Fulbond as a satisfactory alternative to bentonite are most interesting and timely. Some recent refractoriness tests have given the following results :

Bentonite	.	.	.	.	1250° C.
Fulbond No. 1	.	.	.	.	1220° C.
Fulbond No. 3	.	.	.	.	1150° C.
Fulbond No. 2A	.	.	.	.	1140° C.

It is possible that the commercial bentonite deliveries vary in refractoriness, as one large user of Fulbond No. 2A considers it to be more refractory than the bentonite it has displaced. The influence of this characteristic of bonds is under examination in the hot-strength and sintering tests which are in progress.

Since the presentation of the Report the attention of the Sub-Committee has been directed to an increase in the amount of burning-on in a large foundry with a reclamation plant when Fulbond was used in place of bentonite, and also to one or two instances where Fulbond sands tend to dry off and develop friability at a faster rate than bentonite sands. These matters are under close investigation with the collaboration of the foundries concerned, and a full examination of all the factors which might conduce to these troubles is being made. Speaking generally, the various grades of Fulbond are giving satisfactory results when used in place of bentonite in the proportions recommended.

Dr. Skerl rightly emphasises the desirability of adequate technical control in the preparation of core-sand mixtures and of the temperature and time of baking of the cores. It is clear that the optimum stove temperature for individual core binders needs fairly close definition.

The data published on pp. 446 P and 447 P referring to gas evolution from cores were not intended to provide a reference chart for the derivation of the gas evolved from any core mix, but rather to be an indication of an experimental method of determining such data for specific groups of materials and give some preliminary results obtained by its use. The curves in Fig. 14 apply only to the conditions stipulated in the text, namely, silica sand bonded with only one bond, fired at 1000° C. after an initial baking at 205° C. Quite obviously, if the material after baking still contains gaseous condensable constituents which are likely to affect the results appreciably, then the gas must be collected under conditions in which these can be separately collected and determined. This would not present serious experimental difficulties. It is clearly stated on p. 447 P that the derivation of the volume of gas evolved from the loss of weight on heating is no criterion of the volume of gas evolved in the case of core compounds, and it would have been thought that this remark was a sufficient warning to guard against the use of either of the methods for any mixtures in

which the disturbing factors mentioned by Dr. Skerl were likely to arise.

Whilst it would be agreed that gas evolution must always be regarded from the practical standpoint of being a subordinate consideration to that of bonding, if the same bonding characteristics can be obtained by methods which reduce the evolution of gas, then these latter methods must always be preferred.

## Further discussion on

# FIRST REPORT OF THE STANDARD METHODS OF ANALYSIS SUB-COMMITTEE OF THE COMMITTEE ON THE HETEROGENEITY OF STEEL INGOTS.

*Paper No. 11/1942 of the Committee on the Heterogeneity of Steel  
Ingots (submitted by the Standard Methods of Analysis  
Sub-Committee.)*

This Report was presented at the Annual General Meeting of the Institute held on May 7th, 1942, and will be found, together with the correspondence to which it gave rise, in the *Journal of the Iron and Steel Institute*, 1942, No. I., p. 279 P. Later it was discussed at a Joint Meeting of the Institute with the Sheffield Society of Engineers and Metallurgists, the Sheffield Metallurgical Association and the South Yorkshire Section of the Institute of Chemistry held at the Royal Victoria Station Hotel, Sheffield, on Wednesday, June 24th, 1942, at 7 P.M., under the Chairmanship of Dr. W. H. Hatfield, F.R.S. (Vice-President of the Institute and President of the Sheffield Society of Engineers and Metallurgists). The Report was presented by Dr. E. Gregory, Chairman of the Standard Methods of Analysis Sub-Committee; a summary of its contents, the discussion and the Sub-Committee's later reply are recorded below.

## SUMMARY.

In this First Report the Members of the Sub-Committee recommend methods that they have devised, from both theoretical considerations and practical experiments, for the determination of sulphur and of phosphorus in carbon steels.

The recommended method for sulphur is a refinement of the gravimetric *aqua-regia*/barium-sulphate process, and for the determination of phosphorus the Sub-Committee recommends a modified bromide process, whereby arsenic is eliminated before the precipitation of the phosphorus as the yellow precipitate, as nearly all commercial steels contain arsenic.

Precise details of analytical procedure are laid down, and notes are appended drawing attention to the precautions needed to reproduce results within the specified degree of accuracy expected when all practical instructions are rigidly adhered to.

In the case of both elements, the Sub-Committee is unanimously of the opinion that the recommended methods cannot be expected to yield consistent results closer than  $\pm 0.0015\%$  to the true sulphur and phosphorus contents of the steel.

It is emphasised that the methods recommended were devised primarily for "referee" purposes, and, therefore, little cognisance was taken of the time or expense involved in the determination of either element. The main object was to devise standardised processes yielding comparable results when carried out by different chemists using the same samples of steel.

The Report concludes with a recommended method for the determination of lead in steel. This method, based on the separation of the lead as lead sulphate and conversion to lead molybdate, was rigorously tested and remarkably close agreement was obtained.

*DISCUSSION.*

Dr. E. GREGORY (The Park Gate Iron and Steel Co., Rotherham), Chairman of the Standard Methods of Analysis Sub-Committee, presented the Report.

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S., Brown-Firth Research Laboratories, Sheffield): This Report has been presented in a very interesting manner. Since the turn of the century, I should think between 1000 and 2000 million tons of steel have been manufactured and examined for sulphur and phosphorus contents, those elements have been reported on by chemists, and the steel has been accepted or refused, yet to-day the greatest accuracy in the sulphur determination—say, of 0.03%—that can be claimed is  $\pm 5\%$ . I do think that, since you have not attained a very high standard of accuracy, and since this is the best that can be done, it cannot be too widely known; everybody must realise that there is this experimental error in the determination of sulphur and phosphorus, and our specifications must be judged with knowledge of the limitations of even wet analysis.

Mr. B. W. METHLEY (Messrs. Steel, Peech and Tozer, Sheffield): I should like to ask you, Sir, as Chairman of the Committee on the Heterogeneity of Steel Ingots, can you definitely produce a sample of steel so uniform that it would enable us to give results more accurate than those obtained at the present time?

The CHAIRMAN: Yes. If an ingot is sectioned, there is a lenticular zone in the bottom half where the composition is very uniform. I do not question that this Sub-Committee took every precaution to obtain a sample as homogeneous as the advanced art of ingot-making now permits.

Mr. METHLEY: All I asked was, is that sample so homogeneous that we can guarantee an accuracy within 0.003% by chemical methods?

The CHAIRMAN: I think the answer is that it should not be put in those terms, but as I put it, that, of the sulphur present, 0.03%, the greatest limit of accuracy you practically claim is an error of  $\pm 5\%$ .

Dr. GREGORY: I take it that Mr. Methley's main point is, how far is this degree of accuracy influenced by the heterogeneity of the steel?

Mr. METHLEY: Can he (Dr. Hatfield) produce a sample that will be within 0.001% by any method of analysis?

The CHAIRMAN : I hope so, because we can now produce steel of 0.005% sulphur.

Mr. METHLEY : How do you know, if you do not know how to analyse it?

The CHAIRMAN : Quite a weight of steel is being examined during the war with a sulphur content down as low as, shall we say, 0.003, 0.004 and 0.005%.

Mr. J. L. WEST (Messrs. Hadfields, Ltd., Sheffield) : Plus or minus how much—25%? You could not guarantee the 0.004% sulphur nearer than 0.001%, which is an error of 25%.

The CHAIRMAN (to Mr. Stanfield) : I think you examined some of these steels yourself?

Mr. G. STANFIELD (Brown-Firth Research Laboratories, Sheffield) : In one particular case where the figures were very low, three different investigators reported a minimum of 0.003% and a maximum of 0.005%.

Dr. GREGORY : On the question of the limits of accuracy, on p. 283 P of our Report we say that "it will be observed that three investigators reported 0.044% and three others a value of 0.039%, *i.e.*, a range of error of 0.005% of sulphur, which the Sub-Committee considered to be excessive. It was pointed out, however, that the difference between these values indicated the gain or loss of about an eighth of a milligramme of sulphur only, or the equivalent of less than a milligramme of barium sulphate."

The CHAIRMAN : And all those figures depend on the weights you are handling.

Dr. GREGORY : Yes, on the so-called standard weights and on the accuracy of the chemical balance. If we expect to get greater accuracy we are coming down, surely, into the realms of micro-chemical analysis.

Mr. T. E. ROONEY (National Physical Laboratory, Teddington) : In the discussion certain points have been raised about the degree of accuracy which can be obtained. It may be remembered that when the old No. 5 Committee of the Institute was engaged on the preparation of standard samples of steel, the samples were analysed by six district authorities. On the earlier samples there was a wide difference between the maximum and minimum values reported, even between the analyses from the same district. As the work



proceeded, however, and further samples were circulated, the agreement between the analyses became very much better. I think, therefore, that the value of this Sub-Committee lies in the fact that it is going to be, as I hope, a permanent Sub-Committee to examine analytical methods and circulate samples. Such a practice tends to tighten things up and keeps the personnel of the laboratories up to scratch.

It may also be remembered that the No. 5 Committee accepted an agreed figure for the percentage of a particular element in the individual standards and made a plus or minus allowance for variation and error. I think that this is the best way of expressing the tolerance which should be allowed, because, as mentioned by Mr. Methley, there may be some heterogeneity in the steel. The heterogeneity may be well within the 5% referred to in the present Report, but there may be a lot of small factors which, added together, amount to 5%. For instance, quite large errors may occur in weighing, depending on the variation of temperature in the balance room, the condition of the balance and, in particular, the condition of the weights.

There is probably a considerable difference of opinion as to whether the best methods have been adopted by the Sub-Committee, and I think that Dr. Gregory has had a very difficult job in reconciling all the various viewpoints. At the meetings that I have attended there have been long discussions about small details, but a start has got to be made somehow and as time goes on and the work of the Sub-Committee proceeds difficulties will tend to level themselves out.

For instance, we have been discussing whether the sulphur combustion method is stoichiometric or not. I can remember when the phospho-molybdate method was regarded by some chemists as not stoichiometric. The factor for the alkali titration method was obtained on a standard steel, but nowadays the theoretical factor is almost invariably used. I can also remember when the direct combustion method for carbon was quite a novelty, but to-day it is a standard method, and I think the combustion method for sulphur will, in time, be considered as a standard method.

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S.): Do you remember the plus or minus error agreed on those No. 5 Committee samples?

Mr. ROONEY: As a rule only one significant figure was given for the plus or minus error. For the carbon standard with 0.65% of carbon, the figure for error was given as  $\pm 0.01\%$ . For the sulphur standard with 0.027% of sulphur, the figure was  $\pm 0.002\%$ .

In reporting results of analyses, therefore, only two significant figures should be given, as, with a possible error in the second, a third figure is useless.

Mr. G. MURFITT (Messrs. Wm. Jessop & Sons, Ltd., Sheffield) : I have followed this work with very great interest as it has proceeded; the Sub-Committee is to be congratulated on the presentation of this First Report.

On p. 284 P the difficulty of accurately determining the blank on the sulphur method is mentioned. Has the Sub-Committee thoroughly investigated Mr. Bagshawe's method, in which he carries out two determinations, one on 7.5 g. and one on 2.5 g., taking the difference as the sulphur content of 5 g. of sample? The blank on the process, as deduced from these results, would probably be more accurate, as the further difficulty with regard to acid concentration would be to some extent minimised.

The acid concentration can be accurately controlled by the method according to Ibbotson, who recommends that, after evaporating to low bulk, the solution be made up to a definite volume and a fraction collected through a dry filter. This introduces an additional operation, but it avoids the washing, and also allows the method to be used for tungsten steels without modification.

In the notes on p. 286 P the addition of potassium sulphate to low-sulphur steels is advised. I suggest that it would be of advantage to make a similar addition to the blank determination when carried out on the reagents only.

Mr. B. BAGSHAWE (Brown-Firth Research Laboratories, Sheffield) : The method of taking two samples of the same steel, one of 2.5 g. and the other of 7.5 g., the difference being regarded as the sulphur yield from a 5-g. sample, is a practice that I have used from time to time as a means of eliminating the reagent sulphur blank. The reagent sulphur blank is an admittedly weak spot in sulphur estimations on steels; it can only be regarded as a necessary evil, and its replacement by the dissimilar weight method has some desirable features. At the same time this method unfortunately does not by any means solve the problem, as differences of ferric chloride concentration still exist and this may have a considerable effect on the retention of barium sulphate in solution; in other words, in the case of the 2.5-g. sample the precipitation of sulphur would probably be more complete than it would be from a 7.5-g. sample containing an additional 5 g. of iron as ferric chloride in the same total volume.

There is one other point in connection with sulphur, and that is the question of the relative value of the combustion method as against the time-honoured gravimetric method, which is acknowledged to be tedious and can of course be invested with a variety of difficulties, depending on the type of steel to which it is applied; but the fact remains that the acceptance of the combustion process as a primary standard cannot in the very nature of things be considered so long as it continues to depend upon an empirical factorisation through a steel the sulphur value of which has been deter-

mined by some other method. The combustion process certainly has a very useful and honourable place in the busy works laboratory, and it is the earnest hope of the members of the Sub-Committee that stoichiometric exactness may eventually be achieved. The difficulties may not be insuperable; they may possibly be connected with temperature, rate of oxygen-feed,  $\text{SO}_2/\text{SO}_3$  ratio, or efficiency of absorption, and of course several of these factors are interdependent. As a matter of fact, it is not at all certain that we thoroughly understand the chemistry of the absorption. I think that the work that the Sub-Committee has done so far on the determination of the sulphur in alloyed steels and free-cutting steels has shown quite conclusively that the method does not yield stoichiometric results. When isolated claims are put forward that the method is already stoichiometric, without any positive supporting evidence, I think they can be dismissed, on the basis of present knowledge, as wishful thinking.

With reference to the determination of phosphorus, I have heard exception taken to the sentence in the Report which reads "In two instances, the yellow precipitate was weighed as such, in one case by brushing the dried residue from the filter paper on to the balance scoop." The next sentence, however, gives the answer: "Apart entirely from the fact that this introduces an undesirably high factor, this finish is clearly unsatisfactory." It was necessary to put on record that such a method had been tried by the Sub-Committee; in the early days each co-operating chemist used his own method, and this procedure was stated to be in use by one or two of them. It therefore had to be considered, but the Sub-Committee's opinion is that it is unsafe and undesirable, and that is made clear in the Report.

Mr. J. L. WEST (Messrs. Hadfields, Ltd., Sheffield): Brushing the dried yellow precipitate from the paper is a common routine procedure.<sup>1</sup> It is very useful when there is a decigramme or more of yellow precipitate to be weighed and an accuracy of 2% is sufficient, as in determining phosphorus in cast iron. Working on 0.5 g. of sample and assuming a phosphorus content of 0.5%, 3 mg. of yellow precipitate would have to be left on the paper to make the phosphorus 0.49% instead of 0.50%. This procedure must, however, be definitely rejected for referee purposes and also for small precipitates.

Mr. R. BELCHER (Department of Fuel Technology, Sheffield University): With regard to the proposed gravimetric sulphur method, there is no need to let the barium sulphate precipitate stand overnight before filtering. If a few millilitres of picric acid solution are added before adding the barium chloride the pre-

<sup>1</sup> See F. Ibbotson, "Chemical Analysis of Steel-Works Materials," p. 55, lines 8-10. London, 1920: Longmans Green & Co

precipitate may be filtered 15–20 min. later. The results are identical with those of the conventional procedure, in which the precipitate is allowed to stand overnight. The picric acid causes coarse crystals of barium sulphate to form immediately. Why it does so still awaits explanation. The method has been confirmed by a number of workers including myself.

Secondly, it has been suggested that pure sodium phosphate should be used as a standard in the phosphorus determination. Some years ago American investigators showed that the only phosphate which could be relied upon for this purpose was silver phosphate. No other phosphate was found suitable.

Thirdly, some people appear to be uncertain whether the combustion sulphur method is stoichiometric or not, and I think somebody has suggested incomplete absorption in the bubbler as a contributory cause of low results. As you may know, we in the Department of Fuel Technology have devised similar methods for determining sulphur in coal; more recently we have extended these methods to determining sulphur in other materials. Whilst realising that our conditions are somewhat different from those in the steelworks laboratory, I must point out we have no trouble in obtaining stoichiometric results.

Dr. W. C. NEWELL (Brown-Firth Research Laboratories, Sheffield): I think that credit is due to the Sub-Committee for having brought together their ideas and summarised their experience in this form, especially as it is quite evident from the Report that there have been considerable differences of opinion among the Members. I gather that there are some Members of the Sub-Committee who think that arsenic does not interfere with the determination of phosphorus. Surely the Sub-Committee ought by now to be in a position to make a definite statement as to whether or not arsenic does interfere. The large number of figures given in Table II. of the Report were all obtained by arsenic-elimination methods, and they certainly agree well. Had the arsenic elimination been omitted, would similar figures have been obtained for such high-arsenic steels, and, if not, is it established that arsenic elimination is necessary for steels of normal arsenic content?

With regard to the accuracy claimed—within  $\pm 0.0015\%$  of sulphur—it is not high. However, I look upon it not as the limit of accuracy of the method under carefully controlled conditions in any one laboratory, but rather as the limit of accuracy within which different laboratories could be depended upon to report consistently. In accord with generally accepted analytical principles, all the recommended methods are gravimetric. Since most steel analysis is now performed volumetrically, and since these methods are only of recent recommendation, it would seem likely that the Members of the Sub-Committee have not had much opportunity to gain experience with their methods. I would, therefore,



urge that the methods, as now put before us, be used as much as possible. The outcome will then be, I believe, that aids to accuracy will be found, and increased reliance will be placed on the methods.

Mr. D. MANTERFIELD (Messrs. Steel, Peech and Tozer, Sheffield) : It is very disconcerting when we see the results of different chemists' analyses of standard steel samples, not only on the samples concerned in this Report but on other samples which we see from time to time. Doubtless the Sub-Committee will have considerable evidence of results which are not published in the Report, and it has always been my personal opinion that discrepancies in these figures may be due more to difference in the operatives rather than to difference in the methods. I wonder if the Members of the Sub-Committee have tried each other's methods to see what accuracy can be obtained by using another method. In our own laboratories we fix various standards of accuracy and we have various tolerances, but a general tolerance with regard to sulphur and phosphorus is  $\pm 0.002\%$  with ordinary routine methods. It appears to me that if we can get an accuracy of  $\pm 0.002\%$  with routine methods we really ought to get a greater accuracy than  $\pm 0.0015\%$  with a standard method for referee purposes.

With regard to the methods themselves, I wonder if it is necessary to be quite so precise in laying down the details of the methods. For instance, what is the advantage of using potassium nitrate instead of potassium chlorate in gravimetric fixation; what is the advantage of using potassium sulphate in low-sulphur steels as against *N*/100 sulphuric acid, and so on? Those are just two small points. I do not see any advantage, personally, in the two points that I have mentioned.

With regard to the phosphorus method, I should like to express a personal prejudice—that the precipitate which is actually weighed at the finish does not contain any phosphorus. That is no reflection upon its accuracy, but is simply a personal prejudice that one is weighing something which one is not estimating.

Dr. T. B. SMITH (Chemistry Department, Sheffield University) : I should like to emphasise a fact painfully familiar to analysts, namely, that absolute accuracy is unattainable. In the simplest measurement of any kind there is some error, and in the procedures considered there would be, perhaps, a dozen operations with liability to error at each stage. Even in that most precise branch of analysis, the determination of atomic weights, errors exceeding  $1\frac{1}{2}\%$  have been made in comparatively recent times. Clearly they are inherent in the methods employed, and are due neither to lack of manipulative skill nor to the sacrifice of accuracy to speed. It is noteworthy that such results appear to compare unfavourably with those obtained in more straightforward analyses even by beginners. Much larger errors have in fact been observed in the analyses of



technical products by professional analysts, some of whom, it is said, have been classified as "high" and some as "low" analysts, producers favouring the one class and buyers the other.

In the past many standard methods have given a fallacious impression of accuracy merely because one person on repeating the analysis of a particular sample obtains closely agreeing results. It is, however, quite possible that they may be subject to comparatively large, though constant, errors of method. Even if in a particular case the results closely approximate to the truth it still does not establish the reliability of the method, for the apparent accuracy may arise from the compensation of relatively large positive and negative errors. The disadvantages of depending upon such a cancellation are (a) that large discrepancies are liable to result from very slight variations in the procedure of various analysts, and (b) that, even if the compensation is perfect for one material, it may be adversely affected by a variation in the number and proportions of elements other than the one to be estimated. Now, it happens that the gravimetric estimation of sulphur is beset with difficulties of this kind, and, even when the element is present as a major constituent, errors of the order of 1–2% are quite common. Bearing this in mind an error of  $\pm 5\%$  on 0.03% is not surprising. The important thing for the users of analytical data to consider is whether results subject to such an error provide an adequate criterion for their purposes. In view of the immense amount of work which has been devoted to this problem over the course of some decades, it is most unlikely that any short-cut could be found to a really marked improvement. I am inclined to think that if the need were urgent a relatively prolonged investigation might lead to a halving of the error, though probably only by means of an otherwise undesirable elaboration of procedure.

Whilst the combustion method for sulphur can be made virtually stoichiometric for moderately large percentages in other types of material, I do not think that this is true for the determination of traces in steel, and if in a particular case it appears so, this doubtless constitutes an example of the accidental cancellation of errors. To test the absorption and titration stages of the procedure apart from difficulties arising from the actual combustion (*e.g.*, those due to temperature variations, and to the production of large quantities of iron oxide) I have analysed mixtures of pure oxygen with known small additions of sulphur dioxide. With the silver-nitrate/alkali finish the results were markedly low. Decidedly better values were obtained by the iodide-iodate finish, but in actual combustions the advantage might be partially offset by the fact that a small proportion of the sulphur would be present as sulphur trioxide. This proportion would depend on the temperature attained by the gas, and this is subject to considerable variation in different experiments. It is hoped that an extended study of these individual errors may make adequate corrections possible, but at

present it would seem unwise to regard this method as a stoichiometric referee procedure.

With regard to the criticised method of weighing by transfer to the scoop mentioned on p. 281 P of the Report, its comparative grossness is self-evident and I hold no brief for it. It is perhaps worth referring to the magnitude of errors to which the apparently more elegant method of weighing in a crucible is liable. Some medium-sized crucibles can absorb 4-5 mg. of moisture, and variations of 1-2 mg. are of frequent occurrence. Attempts to improve matters by using a specially good desiccant (*e.g.*, magnesium perchlorate) and rapid semi-automatic balances may even lead to larger variations than more usual procedures unless exceptional precautions (*e.g.*, counterpoise weighing) are adopted.

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S.): I think Dr. Smith's contribution is a very valuable one, and it causes me to make the following suggestion. You are a properly constituted Sub-Committee in a National group of Committees. We have our British Standards Institution which is desirous of trying to rationalise analysis. I do think that it would be invaluable to the manufacturing community, both producers and users, if that Institution would bring out standard methods of analysis, and I think we have gone far enough with sulphur and phosphorus to deal with those elements now. It would mean this, that the best of your efforts would be open to criticism, as they are to-night, but you would in a most meticulous manner lay down all the details that you would follow in this standard method, and everybody dealing with that specification would think of the specification of the sulphur or the phosphorus in terms of that particular method of approach. I think you will agree with that, Mr. Methley, as a producer. It is a position we ought to have attained to long ago. We ought to have recognised the multitude of variables that can influence results.

I remember these arguments many years ago, with Arnold and Brearley, Ibbotson and Methley and Saniter. The difficulties that existed then apparently largely exist to-day, and it would be very intriguing indeed if some Member of your Sub-Committee with a retrospective mind could study the development, for instance, of the method of analysing sulphur over the last fifty years and follow the changes in practice that have been adopted.

Let me put my suggestion as a practical proposition to the Meeting, that your Sub-Committee does engage in negotiations with the British Standards Institution with a view to bringing into being a standard method that shall be a method for reference in which a procedure is meticulously laid down.

Mr. G. PARKIN (Messrs. Edward Pryor & Son, Ltd., Sheffield): The Sub-Committee are to be congratulated on their First Report.

It has always been a source of wonder to me that steelworks chemical analysis, which is fundamental in the production of steel and without which reports on heterogeneity and other matters would be valueless, has for so long been treated as the black sheep in iron and steel technology. Whilst for many years certain standard methods for the determination of individual elements have been accepted and employed by most laboratories, the variation in practised detail and technique for any one method has been simply amazing. This state of affairs has led to many discrepancies and needless argument, and no one will question the need for the work which has now been published. Authoritative standard methods are of value in each and every laboratory, and it is hoped that this Sub-Committee will continue the good work already started and in due course turn their attention to the standardisation of methods for accurate and rapid routine analysis. Having due regard to the continuous developments which are now taking place, this work may involve some mechanisation of the chemist, but it should at least provide a sure foundation for the vast amount of iron and steel research, the results of which are, of necessity, based upon material composition.

So far as the methods detailed in the Report are concerned, I have only one or two comments to make. The Chairman has drawn attention to the standard of accuracy claimed for the sulphur determination, and suggests that an error of  $\pm 5\%$  is unusually high. It does appear to be high, but, taken at its real value, what is the practical significance of such an error? It means that a steel analysing 0.030% of sulphur may actually contain 0.0315% or 0.0285% of the element, and I would suggest that in two steels, alike in every other respect, such a difference is quite meaningless. Further, the error quoted can have little significance relative to the range of sulphur content asked for and allowed in steel specifications, and who would to-day reject a cast of steel analysing 0.052% of sulphur where the stated maximum was 0.050%? So far as very low values are concerned, what is the difference between three steels which are identical except for sulphur contents of 0.005%, 0.003% and 0.001%? I have sufficient faith in the chemist to believe that when a controlled sulphur range of 0.003% is found both practicable and advisable, a method meeting the new requirements for accuracy will be forthcoming.

Just one point concerning the actual method for sulphur determination. Has any fundamental work been done on the solubility product of barium sulphate in acid solutions of ferric chloride of varying concentrations of ferric chloride, hydrochloric acid and barium chloride? It would appear that the presence of an excess of barium ions is considered sufficient to ensure complete precipitation of the sulphate. It might, however, be of interest to learn what happens when chemically pure barium sulphate is digested in solutions of various concentrations of the respective

constituents, adjusted to different temperatures. Under particular solution conditions it is possible that the solubility product may reach a value equivalent to 1 or 2 mg. of barium sulphate, and this is of the same order as the blank determination.

Mr. J. L. WEST (Messrs. Hadfields, Ltd., Sheffield) : In "Introduction to Physical Chemistry,"<sup>1</sup> the solubility of barium sulphate in pure water at 18° C. is given as 2.3 mg. per litre.

Mr. PARKIN : What is the solubility product in solutions of acid ferric chloride prevailing at the time of sulphate precipitation ?

Mr. WEST : That raises many other questions, because the art of gravimetric analysis is to prepare a pure substance containing or having some quantitative chemical relation to the element being determined, obtaining 100% yield; you are going to have positive errors due to contamination of the precipitate if excessive means are taken to suppress the amount dissolved, *e.g.*, reduction of volume, and negative errors if no means (such as excess of precipitant) are taken to suppress the solubility.

Mr. E. J. VAUGHAN (Admiralty, Bragg Laboratory, Sheffield) : A very considerable part of the discussion this evening has been centred on the stoichiometric nature or otherwise of the combustion sulphur process. Dr. Smith has dealt with the theoretical considerations very fully, and I would add that the matter has been discussed at length in committee, and a very considerable amount of work carried out, but we were unable, by the normal method, the quick rapid method, which could be completed in some 5 min., to establish a stoichiometric relationship. In this view the Sub-Committee are widely supported in the literature, and for those interested I would refer to a concise summary of the combustion method by Hale and Muehlberg,<sup>2</sup> in which a very complete and detailed study of the possible sources of error appears. Mr. Belcher claims that he has established a stoichiometric relationship, but his work has been carried out on fuels, in which the conditions are very different. A loss of 0.01% on a sulphur content of 1.50% is so small as to suggest a theoretical yield within the limits of experimental error, but a loss of 0.01% of sulphur on a steel containing 0.05% would be a serious matter. The proof that combustion methods for sulphur in other materials are stoichiometric cannot be accepted as proof that the steel sulphur combustion method is also stoichiometric.

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<sup>1</sup> J. Walker, "Introduction to Physical Chemistry," 7th edition, p. 356. London, 1913 : Macmillan & Co., Ltd.

<sup>2</sup> *Industrial and Engineering Chemistry, Analytical Edition*, 1936, vol. 8, Sept. 15, p. 317.



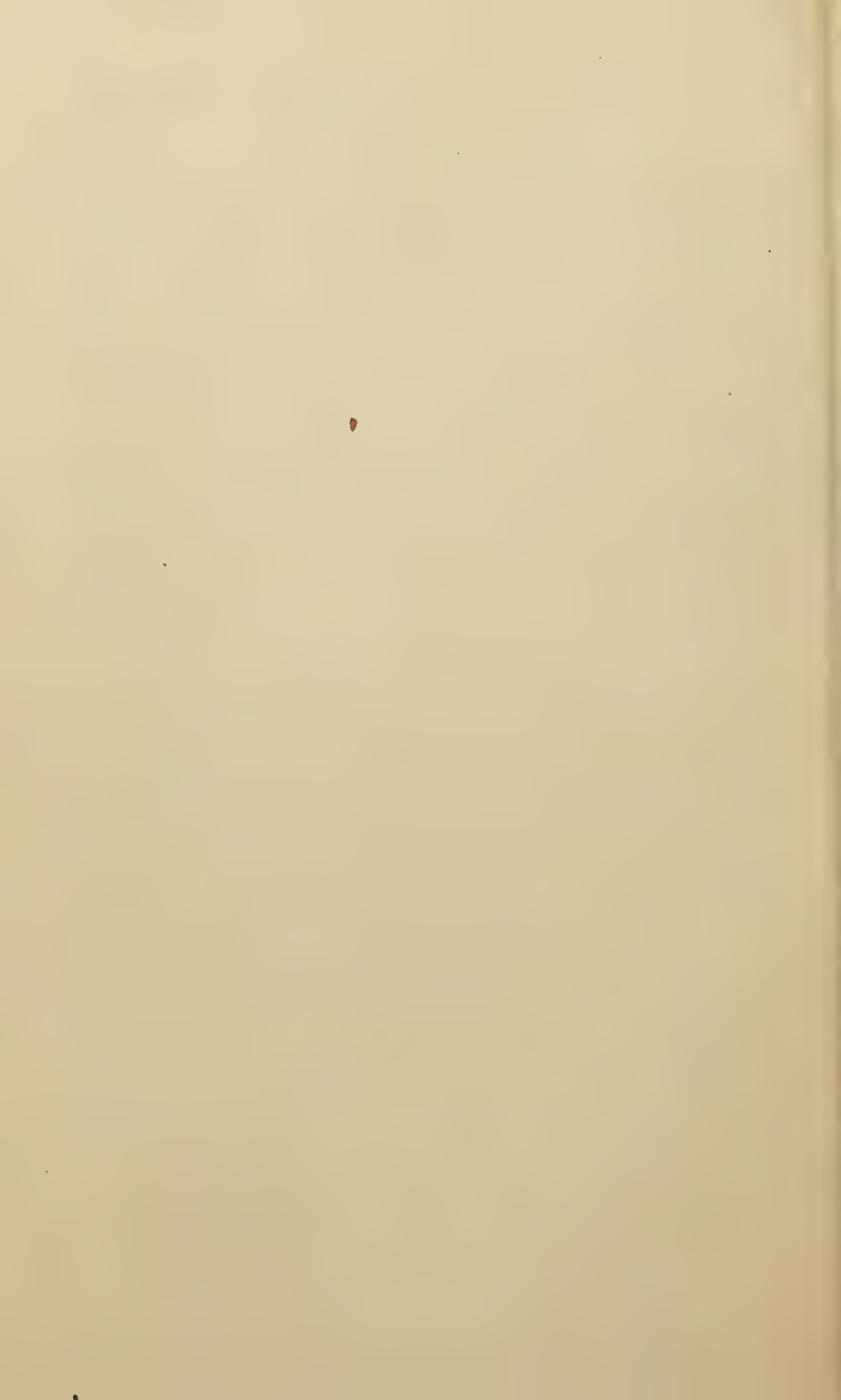
*SUB-COMMITTEE'S REPLY.*

The SUB-COMMITTEE, in reply, wished to express their appreciation of the interest taken in the presentation of the Report at the Sheffield Meeting. Most of the criticisms, however, had been anticipated, and had been satisfactorily dealt with by individual members of the Sub-Committee.

Mr. Belcher's contribution was interesting and, since the meeting, the Sub-Committee had fully investigated the influence of picric acid on the precipitation of barium sulphate. The results indicated that no special advantage would be gained by the addition of picric acid when dealing with the really very small amounts present in most commercial steels.

Dr. Hatfield's suggestion for a historical survey of the development of methods for the determination of sulphur was an excellent idea and would be borne in mind. In regard to negotiations with the British Standards Institution, this has been done and much progress has now been made towards the adoption of the Sub-Committee's processes as standard methods.





## Further Discussion

## ON THE CARBIDE AND NITRIDE PARTICLES IN TITANIUM STEELS.

By WILLIAM HUME-ROTHERY, M.A. (OXON), D.Sc. (OXON), F.R.S.,  
GEOFFREY VINCENT RAYNOR, M.A. (OXON), Ph.D. (OXON), AND  
ALEXANDER TORRANCE LITTLE, B.Sc. (GLASGOW) (INORGANIC  
CHEMISTRY LABORATORY, UNIVERSITY MUSEUM, OXFORD).

This paper was presented at the Annual General Meeting of the Institute held on May 7th, 1942, and will be found, together with the correspondence to which it gave rise, in the *Journal of The Iron and Steel Institute*, 1942, No. I., p. 129 P. Later it was discussed at a Joint Meeting of the Institute with the Sheffield Society of Engineers and Metallurgists, the Sheffield Metallurgical Association and the South Yorkshire Section of the Institute of Chemistry held at the Royal Victoria Station Hotel, Sheffield, on Wednesday, June 24th, 1942, at 7 P.M., under the Chairmanship of Dr. W. H. Hatfield, F.R.S. (Vice-President of the Institute and President of the Sheffield Society of Engineers and Metallurgists). In the authors' unavoidable absence the paper was presented by Dr. A. H. Jay; his presentation of a summary of its contents, the discussion and the authors' later reply are recorded below.

## DISCUSSION.

Dr. A. H. JAY (The United Steel Companies, Ltd., Stocksbridge, near Sheffield), in presenting the paper, read the following summary prepared by the authors, who were unavoidably prevented from attending the Meeting :

## SUMMARY.

The object of the investigation described was to throw light on the relations between those particles in titanium steels which are commonly described as titanium carbide and nitride respectively. We should have preferred to have approached the problem scientifically, and to have worked first with pure iron-titanium-carbon alloys cast in a vacuum, and then to have extended the investigation so as to introduce nitrogen, and other impurities, under controlled conditions. The problem was, however, sent us by the Research Department, Woolwich, and we were asked to explore alloys of commercial purity, and circumstances arising later compelled us to confine the work to this particular batch of steels. In spite of this handicap, a certain amount of progress has been made, and it is satisfactory to note that the microscopic, X-ray and chemical methods have led to results which are in good agreement.

The microscopic analysis made it clear that the constituents of the steels could be divided into those of the genuine carbon-titanium-iron (plus silicon, plus manganese, &c.) system and what we have termed impurity particles, which appeared to have been introduced into the steels by some quite uncontrolled process, since the proportion of these impurity particles varied enormously from one bar to another, and also in different parts of the same bar. In many bars, a considerable percentage of the titanium was clearly present in the form of impurity particles, and we must emphasise that the

diagrams showing the structures of the steels are in no way meant to replace the existing equilibrium diagrams, but merely summarise the structures of this particular batch of steels.

The evidence seems fairly convincing that titanium carbide and nitride form a series of solid solutions, with a whole range of colours extending from the yellow of titanium nitride, through orange and brown, to the grey of titanium carbide. A given bar might contain particles with a wide range of colours, but the general tendency for increasing carbon content to produce a greater proportion of brown or grey particles was very clear. So far as the present work is concerned, there is no evidence for the existence of any cyano-nitrides or other complex compounds apart from the TiN-TiC solid solutions. The presence of slag patches in some of the bars did, however, complicate matters, and a further investigation of pure Fe-Ti-C-N alloys prepared under controlled conditions is much to be desired.

The present results, and also those of the Russian investigators on defective lattices in TiN, suggest that the lattice spacings of TiN, and also of TiC, will be very sensitive to the exact conditions of preparation, and differences between the results of different investigators must be expected.

Continuing, Dr. Jay said: I have already sent in a written contribution<sup>1</sup> to the paper in which was given a brief summary of the work on titanium compounds found in titanium-treated steels. In regard to the detailed findings on the titanium carbide and nitride structures, I do not agree exactly with the authors' findings, but the differences might be explained along the lines of the authors' statement regarding these structures—that the conditions under which the substances are formed determine the dimensions of the atomic structure. In other words, it is difficult to say from dimensions whether the phases are pure or contain small amounts of other elements in solid solution. The phases referred to as impurities were presumably oxides, and from a separated residue containing iron, titanium, oxygen, nitrogen and carbon it is a little difficult to allocate the correct proportions to the particular compounds found by X-ray analysis. My view is that the paper is good so far as it has been possible to examine the problem.

Dr. D. W. DAVISON (Brown-Firth Research Laboratories, Sheffield): In lattice-constant determinations the third place of decimals is well within the limits of accuracy of the method. The widely different values published for TiC and TiN show discrepancies too large to be due to the different investigators and their technique of measurement, and must be attributed to different methods of preparation. The values tabulated on p. 483 p include those given in the present paper.

Knaggs, Karlik and Elam quote a "cyano-nitride"  $\text{Ti}_{10}\text{C}_2\text{N}_8$  with cube side 4.24 Å., but state that it is really a "mixed crystal" of TiC and TiN. The evidence in the present paper confirms this, as there is no new diffraction pattern.

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1942, No. I., p. 140 p.

Value. A.	Determined by—	Source of Information.	Comments.
<i>Titanium Carbide.</i>			
4-29	Van Arkel	{ I. E. Knaggs, B. Karlik and C. F. Elam, "Tables of Cubic Crystal Structure of Elements and Compounds," p. 30. London, 1932: Adam Hilger, Ltd.	
4-31	Brantley and Beckman		
4-315	Hofmann and Schrader		By synthesis.
4-320	...	R. W. G. Wyckoff, "The Struc- ture of Crystals," Supplement to 2nd edition, p. 18. New York, 1935: Chemical Cata- log Co., Inc.	
4-325	Hofmann and Schrader	{ Present paper.	{ From cast iron. From 5.8% Ti, 0.58% C steel.
4-325	Hume-Rothery		
4-60	Becker and Ebert		
		Knaggs, Karlik and Elam, <i>loc.</i> <i>cit.</i> , p. 30.	
<i>Titanium Nitride.</i>			
4-23	...	R. W. G. Wyckoff, "The Struc- ture of Crystals," 2nd edition, p. 228. New York, 1931: Chemical Catalog Co., Inc.	
4-233	Hume-Rothery	Present paper.	
4-40	...	Knaggs, Karlik and Elam, <i>loc.</i> <i>cit.</i> , p. 31.	

The figures on p. 133 P of the paper show that the nitride with the greatest proportion of nitrogen has the smallest lattice parameter. Does this suggest that the compound is more in the nature of a substitutional rather than an interstitial one?

The paper is a welcome demonstration of the value of combining the three methods of investigation when the maximum information is desired.

Dr. W. C. NEWELL (Brown-Firth Research Laboratories, Sheffield): In the absence of the authors, it is very difficult to criticise their paper at all, especially as we all appreciate that Dr. Hume-Rothery has not had the opportunity to make the work as comprehensive and thorough as he would normally have done. The conclusions regarding the nature of the inclusions of titanium carbide and nitride are perfectly reasonable and satisfactory, but I think that the authors themselves would agree that the analytical evidence is rather scant. It would seem that the authors have made a detailed chemical analysis upon the residue from only one of the steels. If this is so then their conclusions as to the atomic ratios are rather premature for publication. The authors' conclusions are supported by evidence brought in from various methods of investigation, and they are thereby given some weight and value to those who can pursue the subject further.

Mr. J. WOOLMAN (Brown-Firth Research Laboratories): All who have to examine the microstructures of steels containing titanium are familiar with the inclusions introduced by this element, and, whilst the presence of these inclusions is not in general seriously detrimental, it is desirable to know their composition. We are indebted, therefore, to Dr. Hume-Rothery for his attempt at the identification of these inclusions. Whilst we are disposed to accept his deductions, it would appear that, on account of the lack of time available for a more detailed examination, there is something to be desired from the point of view of a comprehensive report. For example, the sample of titanium carbide used as a basis for comparison was obtained by electrolytic separation from one of the authors' steels, and it is possible that there may have been some breakdown of the inclusions or modification of them during the process of separation. In any case, it is most probable that the carbide obtained by this method was contaminated by the presence of elements other than titanium and carbon, and it would have been better if an independent source of titanium carbide could have been used as the basis of comparison.

As regards the deductions made from the chemical analysis with reference to the question of the presence of titanium cyanonitride, as it is possible that the conclusions may be affected by the presence in the residues of other materials, repeat chemical analyses on residues from other steels with different titanium contents would be interesting. Apart from titanium carbide and titanium nitride or combinations of the two, other inclusions have been recognised in steels containing titanium. These usually take the form of thin films, which are believed to be mixed oxides of titanium and other constituents. No mention is made of these by the authors.

Dr. JAY: Of the three methods used—X-ray, microscopic and chemical—I believe the X-ray method to be the least troublesome. The patterns of the phases observed are distinct and separate. It is difficult, in view of some uncertainty as to the exact lattice dimensions of the pure compounds, to state the precise nature of the compounds in terms of a possible small solid solution effect.

Mr. WOOLMAN: With reference to Dr. Jay's remarks, the deductions made from the X-ray examinations are based on the size of the crystal lattice. There are a number of titanium compounds, all with the same type of lattice, with only slight differences in the atomic spacings, and which therefore are difficult to identify absolutely if there is some uncertainty about the material used as a basis of reference. I am particularly concerned in this connection with titanium carbide.

Mr. G. PARKIN (Messrs. Edward Prior & Son, Ltd.): There are



two points of possible interest. The authors have dealt with the general mode of occurrence of titanium-compound inclusions, but there appears to be no reference to the sharply defined crystals often found uniformly distributed in steels of low titanium content. Benedicks refers to such inclusions and describes them as pink, but those that I have seen were of a characteristically golden-yellow colour. A good example of such an inclusion is shown in this photomicrograph of a steel containing approximately 0.85% of carbon and 0.15% of titanium. [The print was passed round for inspection.] It is of interest to record that when I showed that same print some years ago to the late Dr. Ibbotson, he immediately remarked "Titanium cyano-nitride, first identified by Sorby in blast-furnace bears!" When he said "cyano-nitride," I don't think that he referred to the definite compound mentioned by the authors on p. 138 P of the paper.

The clusters of haloed titanium inclusions shown in the paper are, it is considered, very similar to the clusters of much lower order often found in titanium-bearing austenitic steels of the 18% chromium, 8% nickel type.

The second point concerns the actual formation of the titanium inclusions. Does titanium act as a nitrogen scavenger in steel, or is the nitride formed in the presence of air during the tapping, &c., of the metal? It would be of interest to know the actual nitrogen contents of the steels investigated and reported upon, compared with the titanium contents. It might be found that the nitrogen values were relatively high, and there might be the possibility of titanium introducing nitrogen into the melt. The absorption of carbon, giving rise to carbide-nitride solid solutions, might occur simultaneously with that of nitrogen, or it might be a secondary process.

Dr. E. GREGORY (The Park Gate Iron and Steel Co., Ltd., Rotherham): I have been very interested in the discussion of this paper. With regard to Mr. Parkin's comment about so-called titanium cyano-nitride, we do get in our blast-furnace bears and also out of "mixer" lining a copper-coloured, highly crystalline, heavy, metallic-looking substance, and I was always under the impression that it was called titanium cyano-nitride. I think that we have some available, and if Dr. Hume-Rothery, Dr. Davison or Dr. Jay would care for a specimen for X-ray examination I shall be only too pleased to let them have it. It may, perhaps, throw some light on this interesting matter.

The CHAIRMAN (Dr. W. H. Hatfield, F.R.S., Brown-Firth Research Laboratories, Sheffield): I personally have listened to the discussion with very great interest. I think that the origin of the work goes back to the Alloy Steel Research Committee, who invited Woolwich to explore the titanium-carbon-iron diagram in

that particular field, and the actual Woolwich research is being done for the Alloy Steels Research Committee. I have not seen the report yet, but it is quite clear that Woolwich have brought in Dr. Hume-Rothery and his colleagues to see whether their method of attack will contribute to their work. It is very interesting to see a brilliant man like Dr. Hume-Rothery come into this most difficult field of investigation. We must admit the brilliancy of a lot of the work he has been doing. You probably all know that we have given a lot of attention to steels containing titanium, but not to such simple steels as the authors are dealing with. When you have much chromium, nickel and other elements as well as titanium, you have a well-nigh impossible proposition to deal with, but Dr. Davison, Mr. Stanfield, Mr. Woolman, Dr. Newell, myself and others have been working in this very complex field, and I am glad to see that Dr. Hume-Rothery has commenced the attack in more simple terms.

Speaking broadly, I think that it can be held that the titanium does essentially combine with the carbide to form titanium carbide. I think that the amount of nitrogen normally present is of a relatively small order. I am not clear what the percentage of nitrogen is in this steel; however, we must not be too critical that the authors have not dealt adequately with that point. They have taken on a very long meticulous piece of work, and it is quite clear that they have carried it on so far in a very interesting manner. The paper has been well worth the discussion that we have given to it this evening.

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#### *AUTHORS' REPLY.*

The AUTHORS replied : We must thank the contributors to the discussion for their interesting comments, and we would say that we fully agree about the need for a more comprehensive investigation. The scientific way to approach the problem would be to work first with pure iron-titanium-carbon alloys and then to introduce the nitrogen and other impurities under controlled conditions. We had hoped to be able to work in this way, but unfortunately this was impossible under the present working conditions, and we had to do our best with one series of steels of commercial purity which was sent to us for examination. It was this factor, and not time, as Mr. Woolman suggested, which led us to discontinue work at this stage. It was felt that we had gone as far as was possible, or indeed advisable, with the material available.

We must admit the possibility of modification of residues during extraction, but feel that it was unlikely to occur under the conditions of our experiments. Contamination certainly occurred to varying extents, as shown by our diffraction patterns, but, since the residues were not annealed after separation, these contaminations would

remain as separate phases and would not, therefore, affect the lattice spacings of the compounds. We agree with Mr. Woolman that an independent standard of titanium carbide is very desirable, but we would emphasise the dangers of working with the so-called synthetic nitrides and carbides prepared by heating titanium in nitrogen or by carburisation of some kind. These products are of very uncertain composition, and, as Dr. Davison points out, of very variable lattice spacing, and require the most careful examination before they are used as standards. They may contain an excess or deficit of one element or the other according to the precise details of the experiments. That is perhaps a reason why it may be a sounder principle to use as standards compounds extracted from selected steels, since the results of the work are intended to apply to the relations between the compounds actually found in complex steels. With regard to Dr. Davison's suggestion that titanium nitride may be to some extent substitutional, we would point out that the observed effects may be due to vacant sites in the skeleton titanium lattice. Only accurate density measurements would settle this question, and specimens in a suitable form are difficult to prepare. We refer Dr. Davison to the paper by A. Brager.<sup>1</sup>

Dr. Newell and Dr. Davison refer to the analytical results. We agree that further analytical evidence would be helpful, but feel emphatically that it should be obtained from residues extracted from carefully prepared pure alloys. The analysis of complicated residues like those that we obtained can give only an average result, especially in view of the diversity of particles observable under the microscope and the lack of uniformity in the steel bars. Such residues may contain some particles of composition quite different from the average, and these only confuse the issue. In the circumstances in which our work was carried out, no residue which we could have hoped to secure would have given less complex results, so that additional work on our specimens would have been of restricted value.

Mr. Parkin raises the question of titanium cyano-nitride. Considerable confusion exists with regard to the substance to which this term has been applied in the past. In view of the formation of solid solutions between titanium carbide and titanium nitride, it seems doubtful whether there is any such thing as a "cyano-nitride" compound to which a name or formula can be assigned. It would probably clarify the situation if this term were allowed to lapse. With regard to the actual formation of titanium nitride in steels, only careful foundry experiments with control analyses can answer the question properly; we have ourselves suggested such experiments.

We are in substantial agreement with Dr. Jay, to whom we are grateful for his kindness in introducing the paper, but it is only right to say that, while we agree about the value of X-ray methods, they were in this case the most confusing of the methods used. The films

<sup>1</sup> *Acta Physico-chimica*, U.R.S.S., 1939, vol. 11, p. 617.

obtained were almost inexplicable until chemical analysis and visual examination of the residues had indicated the presence of slag particles. In this case, therefore, the combination of X-ray methods with those of chemical and microscopical analysis was essential for the solution of the problem. The differences between Dr. Jay's results and our own are almost certainly due to the precise conditions of formation, and the subsequent heat treatments and mechanical treatments should also be taken into account. At the same time, the constancy of the spacing for titanium carbide is suggestive.

In conclusion, we must thank Dr. Hatfield for his appreciative remarks.



## OBITUARY.

FRANK WILLIAM HARBORD, C.B.E., died on December 27th, 1942; he was eighty-two years old. Born on December 8th, 1860, near Norwich, he was the son of J. M. Harbord, who was engaged in business in that city, and of Emily, daughter of William Riches, of Oxwick. He received his general education privately and at St. Olive's Grammar School, and then went to the Royal School of Mines, where, studying under (Sir) Edward Frankland and (Sir) W. Chandler Roberts-Austen, he won the Bessemer Medal in the final examination for the associateship. He graduated in 1882 and in the same year was first prize-man and a silver medallist in the City and Guilds Honours Examination in Iron and Steel Manufacture. He then worked for a short time with Dr. J. E. Stead, of Middlesbrough. He spent the next ten years of his career in iron and steel works in the Midlands, first as metallurgical chemist at the works of Sir Alfred Hickman and the South Staffordshire Steel Ingot Co., Ltd., and then as manager of the steelworks of Messrs. Hatton, Sons & Co., Bilston. This industrial experience was a valuable prelude to the rest of his life, which was devoted to the study of metallurgical engineering and to consulting work. He accepted an appointment as chief chemist to the Government of India and was metallurgist at the Royal Indian Engineering College, Coopers Hill, from 1892 to 1905. In the latter year he went into private practice with the late Edward Riley; with his knowledge and energy he built up one of the best known and most successful firms of consulting metallurgists, Messrs. Riley, Harbord and Law, of which he had been the senior partner for many years at the time of his death.

Mr. Harbord's life coincided with the development of modern methods of steelmaking. The Bessemer converter, which has made possible the production of steel in large quantities, was introduced four years before his birth; he was four years old when the Martin brothers introduced their method of steelmaking. Snelus and others were at work on the problems of dephosphorisation during his boyhood, and he was a student at the Royal School of Mines when Thomas made known his discovery of the basic process in 1878 and when the first basic converters were built at Middlesbrough in the following year. In 1899 the continuous process of steelmaking was introduced in America by his friend, Mr. Benjamin Talbot, who later was to succeed him as President of the Institute. These developments made possible the mass production of steel on which all modern industrial progress is based. Sir (then Mr.) Robert Hadfield's announcement in 1884 of the properties of manganese steel, the introduction of electric steelmaking and the development of the modern alloy steel industry took place during his early manhood; on them modern mechanical engineering



depends. Mr. Harbord followed all these developments keenly; he had himself been associated with the early operation of the basic Bessemer and basic open-hearth processes in the Midlands (hence he was deeply interested in the re-introduction of basic converters into Great Britain half a century later). His firm specialised for a time in metallurgical problems arising out of railway development. Although early papers revealed that he was a skilled analyst, he was always more interested in understanding the principles on which modern steelworks practice is based and in the development for industrial purposes of the new range of products thus made available than in the elucidation of scientific details. He was thus well qualified for his appointment as metallurgist to a Commission which, in 1904, examined the position of electric steel smelting in Europe for the Canadian Government as well as for an investigation into the commercial possibilities of the manufacture of iron and steel in South Africa carried out in 1909 on behalf of the Transvaal Government.

During the war of 1914-1918, he was a Member of the Ordnance Committee and acted as Honorary Advisor in Metallurgy to the Ministry of Munitions and in 1918 was awarded the C.B.E. and made an Officer of the Legion of Honour.

Mr. Harbord was a member of numerous scientific societies; he was a Past-President of the Institution of Mining and Metallurgy, a Member of Council of the Institute of Chemistry for two three-year periods and a Member of the Iron and Steel Industrial Research Council. He served on several committees and panels of the British Standards Institution and was a Member of the Council of Honour of the International Air Congress, 1923. He joined The Iron and Steel Institute in 1884, became a Member of Council in 1916, a Vice-President in 1924, and President in 1927-1928. In 1916 he was awarded the Bessemer Gold Medal, the highest distinction that the Council has in its power to award.

Mr. Harbord wrote a number of important papers on the metallurgy of steel, and with Mr. J. W. Hall, he was the author of the standard text book "The Metallurgy of Steel," which ran into seven editions and was the best general work on this subject at the time of publication. To The Iron and Steel Institute he contributed the following papers :

"Some Preliminary Experiments on the Removal of Metalloids in the Basic Siemens Furnace." (*Journal*, 1886, No. II.)

"On the Effect of Arsenic on Mild Steel." (With A. E. Tucker; *Journal*, 1888, No. I.)

"A Note on the Presence of Fixed Nitrogen in Steel." (With T. Twynam; *Journal*, 1896, No. II.)

"The Relation between the Process of Manufacture and Some of the Physical Properties of Steel." (*Journal*, 1907, No. I.)

"Presidential Address." (*Journal*, 1927, No. I.)

"The Thomas-Gilchrist Basic Process, 1879-1927." (*Journal*, 1937, No. II.)

He was a frequent speaker at Meetings of the Institute and his courteous criticism and advice were freely given both to the Council, to the staff and to Members.

During the last years of his life he suffered from increasing blindness, but in spite of this serious handicap and numerous operations undergone in the vain hope of improving his sight, he attended regularly at his office until the last few months, and up to the very end retained his lively interest in metallurgical progress and the fortunes of the technical institutions with which he was associated. Those who had the good fortune to know him will look back with pleasure to the help that he was always so willing to give and will recall with gratitude the memory of a distinguished scientist and a kindly personality.

Dr. CHARLES EUGÈNE SCHNEIDER died at his home in Paris on November 17th, 1942; he was seventy-four years old. Born at Le Creusot on October 28th, 1868, he was a grandson of the founder of the Schneider firm, who, about the beginning of last century, bought the old Royal Ironfoundries at Le Creusot and laid the foundations of a business which came to exercise a dominating influence in the engineering and armament industry of France and at one time in many parts of Central Europe. Having completed his general and technical education, Monsieur Schneider was apprenticed to his father, the late Monsieur Henri Schneider, and in 1887 became a partner in the firm; on the death of his father in 1898 he became the sole head of the Company. He set about extending the range of manufactures and the scope of the concern and adopted a system of specialisation in the various works; the business developed and prospered greatly, and by the outbreak of the 1914-1918 war it had been equipped to deal with all kinds of war equipment, as well as railway work, locomotives, boilers, turbines, mine gear, ships, &c. He was always in close touch with the Government of his country, and was a member of the Chamber of Deputies from 1896 till 1910. During the last war British and French iron and steel interests were, of course, drawn closely together in the common war effort, and Monsieur Schneider paid frequent visits to Great Britain.

In 1919 Monsieur Schneider was appointed head of a French Government Mission sent to America. He was well received by the United States steel industry and was accorded many honours; he received the Gold Medal of the Mining and Metallurgical Society of America, was elected an Honorary Member of the American Iron and Steel Institute, was made a Freeman of the city of Pittsburgh and was awarded the degree of Doctor of Science by the University of that city.

On returning to France, his next problem was to adapt his Company to the new conditions of post-war Europe; among other branches of engineering he took up the building of oil engines for

motor ships and submarines, and he interested himself in the growing schemes for the electrification of France by developing her water and steam power-station resources. On the financial and administrative sides his organisation had already been extended to cover not only France and her Colonies but also other European countries, and, besides new French industries, he acquired important interests in the Luxemburg iron and steel industry and in Central Europe; in particular, financial control of the Skoda Works as well as mining and steel interests in Poland and Hungary were obtained, but the Skoda Works were returned to the Czechoslovakian Government some years ago.

Monsieur Schneider's association with The Iron and Steel Institute was of long standing. Elected a Member in 1890, he became a Member of Council in 1905 and a Vice-President in 1915. During 1918-1920 he was President and held that office with distinction; in those two years he learnt to know well the leading personalities in the British iron and steel industry. Primarily an industrialist, he wrote few technical papers; the following were his contributions to the proceedings of this Institute:

"Presidential Address." (*Journal*, 1918, No. I.)

"An Investigation of Various Forging Operations Carried out under Hydraulic Presses." (*Journal*, 1920, No. II.)

"An Investigation of Hot-Drawing on the Mandril." (*Journal*, 1921, No. II.)

At the Annual General Meeting of the Institute in May, 1930, in the presence of Monsieur de Fleuriau, the French Ambassador, he was presented with the Bessemer Gold Medal in recognition of his distinguished services in the advancement of the technology of iron and steel manufacture and the science of metallurgy; in acknowledging the honour, the highest that the Council of the Institute could bestow, he spoke feelingly of the work of the Institute and of the years when he had served as its President, and recalled that his father had been awarded the same Medal in 1889.

In 1934 he was elected to a seat in the Académie des Sciences Morales et Politiques which had become vacant on the death of the late Monsieur Louis Lépine.

He was also a Member of the Institut de France.

In developing his vast enterprises Monsieur Schneider did not lose sight of the human element, and his care for his workmen and staff and the provision of good living accommodation and opportunities for leisure were always matters of personal interest to him.

Death has thus removed a striking figure from the industrial life of France and one who, during long years of close association with the iron and steel industry of Great Britain, had played a leading part in the scientific development of metallurgical research and practice.

WATSON ALLEN died on March 29th, 1942, aged fifty-one.

About thirty-seven years ago he joined the staff of the Park Gate Iron and Steel Co., Ltd., of Park Gate, near Rotherham, as an office boy; progressing in the company's service, as a result of his native ability, initiative and devotion to duty he held a number of responsible positions and about fifteen years ago was appointed manager of the bar mills, which position he held at the time of his death.

Mr. Allen was elected a Member of the Institute in 1936.

Dr. FREDERICK M. BECKET died on December 1st, 1942; he was sixty-seven years of age. A native of Montreal, he studied at McGill University, where he graduated with a Bachelor of Science degree in 1895, and at Columbia University, where he received a Master of Arts degree in 1899. In 1906 he became associated with the Union Carbide and Carbon Corporation; he was formerly president of the Union Carbide and Carbon Research Laboratories, Inc., and a former vice-president of the Union Carbide Co., the Electro-Metallurgical Co., and Haynes Stellite Co., all units of the above-mentioned Corporation, to which he was a consultant at the time of his death.

For many years he was a contributor to technical publications in the chemical and metallurgical fields. Soon after the turn of the century he originated and commercialised the fundamental principle of producing low-carbon ferro-alloys and alloying metals by reducing ores in the electric furnace with silicon instead of carbon. He was the first in America, and probably in the world, to make ferro-vanadium by silicon reduction in the electric furnace; others of his products were ferro-tungsten of commercial quality prepared direct from the high-phosphorus domestic ores, ferromolybdenum prepared direct from the natural sulphide, chromium and manganese metals almost free from iron, silicon metal, and, most important of all, low-carbon ferro-chromium. In 1918 he developed the electric-furnace technique of producing ferro-zirconium, then used for light armour plate and now widely employed for improving the quality of high-grade steels.

For his achievements in metallurgy he received the Perkin Medal of the Associated Chemical and Electrochemical Society in 1924, the Acheson Medal of the Electrochemical Society in 1934, the Elliott Cresson Medal of the Franklin Institute in 1940 and a "Modern Pioneers" award of the National Association of Manufacturers in the same year. In 1929 Columbia University bestowed upon him the Honorary Degree of Doctor of Sciences, and in 1934 McGill University conferred the Honorary Degree of Doctor of Laws on him.

Dr. Becket was President of the Electrochemical Society in 1926, and was elected an Honorary Member in 1934; he was also President of the American Institute of Mining and Metallurgical Engineers in 1933, and of the Chemists' Club in 1939. He was a member of



numerous American Societies, including the American Association for the Advancement of Science, the American Institute of Mining and Metallurgical Engineers, the American Chemical Society, the Electrochemical Society, the Mining and Metallurgical Society of America, the American Society for Metals, the American Institute of Chemical Engineers and the New York Academy of Sciences. He joined The Iron and Steel Institute in 1912.

JOHN WILLIAM BINGHAM died on September 27th, 1942; he was sixty-nine years old. He was a director and the works manager of the Sheffield Forge and Rolling Mills Co., Ltd., steel forgers, rollers, drawers and tilters; he had been associated with the firm for thirty-seven years, having joined the staff originally as a sheet roller. He joined The Iron and Steel Institute in 1915.

EDGAR MIDDLETON BOOTE died on May 15th, 1942, at the age of fifty-nine. Born in Bradford in 1883, he received his early education at the Central Higher School, Sheffield; thence he went to the University College (now the University) of Sheffield to take the full engineering course, and later entered the Metallurgical Department, where he gained an Associateship in Metallurgy in 1907. During the next twelve years he was engaged in the laboratories of several important Sheffield steelworks, and became manager of the crucible melting department of Messrs. Samuel Osborn & Co., Ltd. In 1911 he was appointed chief chemist and metallurgist to the London General Omnibus Co., Ltd., Walthamstow factory (which in the following year became the Associated Equipment Co., Ltd.); among other duties he had charge of the foundry for aluminium and other non-ferrous metals and the heat-treatment department, and also acted as consultant to all the companies included in the group. In April, 1917, he became manager and metallurgist of the Martino Treating and Testing Works at Coventry, which position he held until the works closed down in 1921. His next post was as district manager for the Poldi Steel Co. (England), Ltd., and seven years later he became technical representative of The United Steel Companies, Ltd. In 1931 he took up various appointments in a similar capacity with prominent manufacturers of steel forgings, castings, springs, &c.; at the time of his death he was engaged with Messrs. James Booth & Co. (1915), Ltd.

Mr. Boote was a Member of Council of the Institution of Automobile Engineers and of the Junior Institution of Engineers (a Past-Chairman of the Midland Section of the latter Society), a Past-President of the Coventry Engineering Society and the Birmingham Metallurgical Society, and a member of the Royal Society of Arts, the Royal Aeronautical Society, the Institute of Metals and the Institute of British Foundrymen.

Mr. Boote was a Life Member of The Iron and Steel Institute, which he joined in 1918.



HAROLD BUTLER, M.B.E., J.P., died on December 24th, 1941, in his sixty-sixth year. Born in Halifax, he received his early education there and at the Yorkshire College, Leeds, and at the age of seventeen he entered his father's business, Messrs. J. Butler & Co. In 1908 the commercial management of the firm was largely in his hands, the practical side being in the care of his brother, the late Mr. Herbert Butler. In 1919 the company was converted into the Butler Machine Tool Co., Ltd., with the brothers as directors; in 1937 it became a public limited company and Mr. Harold Butler was appointed chairman and managing director. During his lifetime Mr. Butler saw the business grow from a small concern, occupying converted premises, to one of the largest machine-tool firms in Great Britain, with extensive buildings designed specially for the large-scale production of machine tools. Under his guidance, by concentrating on one particular type of machine, the company developed a fine reputation for machine tools of the reciprocating type, the extent of which was due almost entirely to Mr. Butler's efforts.

During the war of 1914-1918 Mr. Butler was a member of the Halifax Munitions Board, and his company produced large quantities of munitions as well as of machine tools; he was awarded the M.B.E.

Mr. Butler was a founder member of the local branch of the Foreman's Mutual Benefit Society, of which he was Chairman from 1918 to 1920. In 1920-1921 he was President of the Halifax District Engineering Employers' Association. He was also a founder member of Associated British Machine Tool Makers, Ltd., and was chairman of the board in 1922-1923 and from 1932 to 1935. In 1930-1931 he was President of the Halifax Chamber of Commerce. In 1938 Mr. Butler became President of the Machine Tool Trades' Association and continued in that office until March, 1941.

Mr. Butler joined The Iron and Steel Institute in 1903.

HERBERT JOHN DAVEY, M.B.E., sole proprietor of Messrs. Davey and Bell, inspecting engineers, died suddenly on December 13th, 1941, at Surbiton, Surrey. Born on October 31st, 1875, he left school at an early age and joined Messrs. David Kirkaldy & Son, where he received a sound technical and commercial training under the late Mr. David Kirkaldy, and, during over twenty years service with that firm, acquired a varied experience which was very valuable to him in later years. In 1914, after the death of Mr. Kirkaldy, he started his own practice as an inspecting engineer; after the outbreak of war he took a partner, Mr. A. E. Bell.

In 1915 Mr. Davey joined the staff of the Director of Inspection of Gun Ammunition (Technical) and remained in the Fuze Division until December, 1918; he was awarded the M.B.E. for his services. Shortly after the war the partnership was dissolved and Mr. Davey continued his work as an inspecting engineer. He was responsible

for the workmanship and quality of materials in many well-known buildings, including, in recent years, the "News of the World" building in Bouverie Street, London, E.C., the Bankers Clearing House, King William Street, E.C., the Midland Bank, Manchester, and a number of aerodromes in different parts of the country. He also carried out a considerable amount of inspection work abroad for English companies and knew intimately every steelworks in Europe which carried on trade with Great Britain. In 1937, while still carrying on his own practice, he returned once more to the Fuze Division and remained there until his death.

Mr. Davey was one of the founder members of the Institution of Engineering Inspection (then the Technical Inspection Association), and was for many years a Member of the Council of that Institution and President for the years 1927-1928. He was also an early member of the Institution of Structural Engineers (then the Concrete Institute). Mr. Davey represented the British Iron and Steel Federation on a number of Committees of the British Standards Institution. He was elected a Member of The Iron and Steel Institute in 1939.

JOSEPH LOUIS GASTON DESCHAMPS died at Hitchin on December 15th, 1941, after a long period of ill-health. Having graduated at Liège University, Belgium, he went to Letchworth in 1915 as a young engineer and worked in the shops and foundry of Messrs. Kryn and Lahy in various capacities until 1917, when he became assistant general manager. In 1919 he left, but returned after three months to become general manager. When the new company Messrs. Kryn and Lahy (1928), Ltd., was formed, he and the late Mr. Abel were appointed joint managing directors, and Mr. Deschamps was holding this position at the time of his death. He was one of the leading authorities in Great Britain on the manufacture of steel castings.

Mr. Deschamps became a Member of the Institute in 1924.

HANS JOHAN UNO FORSBERG died on March 23rd, 1941, at the age of sixty. Born at Arbrå in Sweden, and son of a master smith, Mr. Forsberg acquired his early education at Gävle and, after graduating in 1901, he attended the Tekniska Högskola until 1906, when he qualified as a mining engineer. He was immediately successful in obtaining an appointment at the Kungl. Tekniska Högskolans Materialprovvningsanstalt (Testing Department of the Royal Technical College). The work at this institute had an important influence on his future activities. In 1909 he travelled in England and Germany, visiting steelworks and many testing laboratories, and was able to spend a term at Sheffield University studying metallography. The following year he became engineer to the forge at Leufsta Bruk, where for a time practical forging work took the place of more theoretical metallography. The scope at this

works was too limited, however, with the result that in 1912 he applied for, and obtained, the position of manager to the then contemplated testing and research laboratory of the Svenska Kullagerfabrik, soon to become known throughout the world as SKF. With the active support of Sven Wingquist, principal of that firm, a modern laboratory was built. In a surprisingly short time, thanks to Mr. Forsberg's capacity and energy for research, an ordered scheme of dealing with steel analyses, specifications and methods of testing and control was in operation. After two years' work in the laboratory, he became chief engineer to the works. By this time his outstanding qualities were well appreciated by the board of directors, who sent him to the United States of America in 1915 to erect and put in production a ball-bearing factory at Hartford, Connecticut. Returning to Sweden in 1918, he was made technical director and deputy managing director of SKF. In 1938 he became managing director. From 1934 to 1937 he was also manager of Hofors Bruk. The phenomenal development of the SKF concern under the leadership of Mr. Forsberg is too well known to require comment. Hofors Bruk is the company supplying the steel requirements of SKF and, by the direct and indirect influence of Mr. Forsberg's activities, its production methods were rationalised and the steelmaking capacity was trebled. The improvements made under his direction included the introduction in 1929 of the charging of the blast-furnace with 100% sintered ores, the transfer of hot metal direct from the blast-furnaces to the open-hearth furnaces, the erection of a charcoal-drying plant, and in 1934 the erection of a complete new hot rolling-mill. Among his later undertakings was the construction in 1937 of two 15-ton electric-arc furnaces to make steel by a duplex process of his own to suit the special conditions at Hofors.

Apart from his SKF activities, Mr. Forsberg took an active interest in Swedish economic and civil affairs, especially in the later years of his life. He was on the board of several companies, including Skandinaviska Banken A/B, Trafikaktiebolaget Grängesberg-Oxelösund, A/B Bofors and Gamlestadens Fabrikers A/B. He was Vice-Chairman of Sveriges Industriförbund (Federation of Swedish Industries), Member of Council of Sveriges Verkstadsföreningen (Swedish Engineering Association), of Järnbruksförbundet (Iron-works Association), of Svenska Arbetsgivareföreningen (Swedish Employers' Federation), of Ingeniörsvetenskapsakademien (Engineers' Academy of Science) and deputy on the board of Jernkontoret. He was also Vice-Chairman of a national association for the preservation of Swedish culture abroad.

He was elected a Member of The Iron and Steel Institute in 1926.

GEORGE BASIL GARRETT was killed in a railway accident near Dickerson Ma., U.S.A., on September 24th, 1942; he was forty-  
1942—ii

nine years of age. He graduated from the Case School of Applied Science in 1915, and soon afterwards joined the staff of Messrs. Arthur G. McKee & Co., Cleveland, builders of blast-furnaces and steel plants, and at the time of his death was sales manager of the iron and steel division of the company. He made many friends in England, having spent a number of years in this country in the interests of his firm. His father, who was a Member of The Iron and Steel Institute for a number of years, was the inventor of the Garrett mill.

Mr. Garrett joined the Institute in 1920.

DAVID K. GLASS, who died on March 23rd, 1942, was an authority on coke-oven and blast-furnace practice. He started his career with the Carron Company; after the war of 1914-1918 he joined Messrs. James Dunlop & Co., Ltd., and was retained as chief engineer when the steel interests of that concern were merged with Messrs. Colvilles, Ltd. He was actively concerned with the development of Cardowan colliery and with the planning and erection of the hot-metal plant at Messrs. Colvilles' Clyde Ironworks, of which he was at one time general manager.

Mr. Glass became a Member of the Institute in 1937.

WALTER STUART GOODISON died on February 13th, 1942; he was sixty-two years of age. Born in Sheffield on January 20th, 1880, he was educated at Penistone Church School. He started work as a clerk in the Penistone offices of the London and North Eastern Railway (then the Manchester, Sheffield and Lincolnshire Railway, later to become the Great Central Railway). In 1897 he left that employment, and took up a post with Messrs. J. Grayson Lowood & Co., Ltd.; after holding various positions with the firm, he eventually became managing director, which appointment he relinquished about two years ago owing to ill-health.

Mr. Goodison was elected a Member of the Institute in 1934.

FRANCIS JOHN HEMMING died on November 10th, 1941, after a long illness; he was in his fiftieth year. Educated at King Edward's School, Birmingham, he commenced his business career with Messrs. F. H. Lloyd & Co., Ltd.; he also gained experience in metallurgical work in the laboratories of the Patent Shaft and Axletree Co., Ltd. The outbreak of the first Great War cut short his studies, however, and he completed four years of service, first with the Fifth Battalion of the South Staffordshire Regiment and later with the Army Cyclist Corps; he held the rank of major. Resuming his business activities in 1918, he was appointed a director of Messrs. Lloyd's; in 1926 he became second in command to the late Mr. D. C. Lloyd, whom he succeeded in 1931 as managing director. At his death he was chairman and managing director of the company.



Mr. Hemming was a Past-President of the Birmingham Branch of the Institute of British Foundrymen, and a member of the Birmingham Management Board of the Engineering and Allied Employers' Association and of the Executive Committee of the General Steel Castings Association, which body he represented on the Council of the British Cast Iron Research Association. He was a strong supporter of technical education; he was a member of the West Midlands Advisory Council and the Staffordshire County Council College Committee.

Mr. Hemming was elected a Member of The Iron and Steel Institute in 1933. He was for a number of years an active Member of the Steel Castings Research Committee.

GEORGE CHRISTOPHER LLOYD, formerly Secretary of The Iron and Steel Institute, died on July 10th, 1942, after a few days' illness; he was in his eighty-second year. Born on April 30th, 1861, he was the second of four sons of the late Reverend Charles A. Lloyd, Rector of Rand, Lincolnshire. He received his early education from his father and then spent some years at the Moravian School at Königsfeld in Baden. On his return to England he served a five-years' apprenticeship with Messrs. Robert Stephenson & Co., of Newcastle-on-Tyne. Until 1891 he served as a marine engineer, obtaining a Board of Trade Extra First Class Engineer's Certificate and sailing with Messrs. Lamport & Holt of Liverpool and with the Spanish Royal Imperial Steamship Co. "Compañía Transatlántica" to Central and South America, the East Indies and China. The next few years were spent with various engineering companies in London and Glasgow. He represented the Mirrless Watson Co., Ltd., in Austria, France and Germany, and later joined the staff of Messrs. Jeremiah Head & Son, now incorporated in the Wellman Smith-Owen Engineering Corporation, Ltd.

In 1900, when thirty-nine years of age, he joined the staff of The Iron and Steel Institute. This was to become his life's work, for, with the exception of four years spent as Secretary of the Institution of Electrical Engineers, his connection with The Iron and Steel Institute was maintained for over forty years. He served as Secretary from 1909 to 1933 and was nominated Honorary Secretary on his retirement. His period of office as Secretary covered the prosperous pre-war years, the war of 1914-1918 and the difficult years that followed; under his wise guidance the Membership increased as the result of service rendered; the number and importance of papers published was maintained; the Library was greatly extended and the abstraction of British and Foreign literature was put on a proper basis; the Institute began to take a lively interest in co-operative research. It was, however, in maintaining and extending the foreign connections of the Institute that Mr. Lloyd's best work was done, for he was fluent in several languages. Official visits were paid to Canada and the United



States as well as to Austria, Belgium, Czechoslovakia, France, Luxemburg, Italy, Spain and Sweden, and on these, as on many other occasions, he represented the Institute with modest dignity and native charm.

Mr. Lloyd was a member of Council of the Chartered Institute of Secretaries, a Vice-President of the International Association for Testing Materials, and Joint Secretary of the Empire Mining and Metallurgical Congress held at Wembley in 1924. He published the Annual Statistical Reports of the Iron, Steel and Allied Trades Federation from 1915 onwards until the National Federation of Iron and Steel Manufacturers took over this duty, when he joined the Statistical Committee. He was also a Member of the Statistical Committee of the Imperial Mineral Resources Bureau. In 1918 he prepared the first edition of *The Report on the Sources and Production of Iron and Other Metalliferous Ores Used in the Iron and Steel Industry of the United Kingdom* at the request of the Advisory Council of Scientific and Industrial Research. Among honours conferred upon him were the Legion of Honour and the Swedish Order of the North Star.

By Mr. Lloyd's death his many friends among the Members have been deprived of one whom they all, young and old alike, held in affectionate respect. Most of those now living will remember him as he was in later years, when his hair had turned white and his bearing was a little less erect—a courteous, dignified gentleman, typical of an earlier generation; but in his prime he had been a tall and distinguished man with black hair and moustaches, a strikingly handsome and vigorous personality. He never looked his age, and to the very last retained his physical strength to a remarkable degree, while his intellect remained unimpaired. After his retirement he continued to take a kindly interest in the activities of the Institute, where he could often be seen taking a short rest in the Library during one of his visits to town. He always took the greatest interest in the welfare of his staff, who mourn his loss no less than his many other friends.

FRANCIS CHARLES MOSS, J.P., died suddenly on June 17th, 1942; he had been at business on the day of his death, when he attended a meeting of his board of directors. He was fifty-six years of age. After receiving his education at Rotherham Grammar School and Sheffield University, he served an apprenticeship with Messrs. Marshall, Sons & Co., Ltd., of Gainsborough; in 1907 he joined the staff of the Rotherham Forge and Rolling Mills, Ltd., and eventually became managing director.

Mr. Moss was a member of the Institute of Metals; he was also a Justice of the Peace, and he held various positions in connection with the social and administrative affairs of the Wickersley district, near Rotherham, where his home was situated.

Mr. Moss joined the Institute in 1928.

GEORGE L. NORRIS died on April 13th, 1942; he was seventy-six years old. Graduating from Massachusetts Institute of Technology in 1887, he became associated with the Pennsylvania Steel Co., the North Chicago Rolling Mills, the Illinois Steel Co., the Pencoyd Iron Works, the Reading Iron Co., the Walter A. Wood Harvester Co., the Great Northern Railroad, the Laconia Car Co., the McNeil Pipe and Foundry Co. and the Standard Steel Works at Burnham, Pa., where he was engineer of tests. In 1909 he joined the American Vanadium Co., and was one of the pioneers in the development and application of vanadium; he remained with the company when it became the Vanadium Corporation of America, and was still actively engaged as chief metallurgist at the time of his death.

Mr. Norris was Chairman of the New York Chapter of the American Society for Metals in 1921. He joined The Iron and Steel Institute in 1924.

DAVID ROSS died on October 23rd, 1942, in his fifty-seventh year. Formerly manager of the British Mannesmann Tube Co., Ltd., at Newport, Mon., he first went to Tees-side about eighteen years ago to superintend the new tube industry at the Malleable Works of the South Durham Steel and Iron Co., Ltd., of which he became general works manager.

Mr. Ross took a special interest in technical and higher education, and was a Governor of the Stanton Secondary School.

Mr. Ross became a Member of the Institute in 1928.

THOMAS HENRY SANDERS died on January 2nd, 1943. Born in London in 1883, he was one of the first boys to take the London County Council Scholarship presented by the late King Edward VII. (then Prince of Wales). When nineteen years old he commenced his career as an inspector for railway materials under the late Mr. George Cawley, consulting engineer to the Imperial Japanese Railways, and this entailed extensive travel abroad. At the age of twenty-five he received the prize of the year as graduate of the Institution of Mechanical Engineers. During the first Great War he was engaged in the production of war material, first with Messrs. Brown Bayley's Steel Works, Ltd., and then with Messrs. Owen and Dyson, Ltd., railway wheel and axle makers. In 1920 he was responsible for the layout, equipment and management of a spring works for Messrs. Brown Bayley's at Farnley, near Leeds. In 1923 he joined Messrs. Jonas Woodhead and Sons, Ltd., as technical engineer; in 1935 he was appointed technical director, and later was elected a director of the associated companies Messrs. Willford & Co., Ltd., and Messrs. Ibbotson Bros. & Co., Ltd.

Mr. Sanders was a member of the Institution of Mechanical Engineers, of the Institute of Metals and of the Institution of Locomotive Engineers; twice he was awarded medals for papers

read before the latter body. He was a Past-President of the Railway Locomotivemen's Craft Guild (Leeds Centre); in 1931 he was presented with the Freedom of the Sheffield Spring Trade Technical Society.

Mr. Sanders was a leading authority on springs and was responsible for a number of patents. His first text-book on this subject appeared in 1920, and in subsequent years he published further volumes covering the same field, the last of which was completed only a few days before his death. He was in great demand as a technical lecturer, for he was always ready to share his knowledge with others; he did not confine himself to suspension subjects only, for he was also an authority on railway practice all over the world.

Mr. Sanders took up membership of the Institute in 1922.

RALPH PERCIVAL SMITH died on March 19th, 1942. Born in Edinburgh, he received much of his education in Sweden and Germany, and graduated at Charlottenburg. He joined the staff of the Lanarkshire Steel Co., Ltd., in 1908, and twelve years later he entered the works of Messrs. Colvilles, Ltd. In 1928 he moved to Sheffield and took a post in the steelworks of Messrs. Steel, Peech and Tozer (a branch of The United Steel Companies, Ltd.), later becoming a director and general manager of the company's works at The Ickles and at Templeborough.

Mr. Percival Smith was a recognised authority on the manufacture of steel by the open-hearth process and had exceptional personal knowledge of steelmaking on the Continent, in Sweden and in America. At his death he had been for many years Chairman of the Open-Hearth Committee and Conference of The Iron and Steel Industrial Research Council. In this capacity he was responsible more than any other individual for breaking down old-fashioned ideas of secrecy and bringing about that state of intimacy and confidence which now enables open-hearth managers freely to interchange problems and information. The value of this is now so generally accepted that it is difficult to remember that when the Open-Hearth Committee was set up in 1930 many managers and companies hesitated to mention matters which they considered affected operations at their own works only. His friendly courtesy in presiding at conferences made it easy for representatives of other works to join in discussion and the example he gave in disclosing new developments often shamed less enterprising colleagues into emulating his example. He was himself always ready to try out new suggestions and the lead he thus gave encouraged others.

Mr. Smith was a Member of a Sub-Committee appointed by the Council of The Iron and Steel Institute to organise the Symposium on Steelmaking held in May, 1938, and he contributed to it a paper on "Making Basic Open-Hearth Steel for Many Purposes" (*Iron and Steel Institute*, 1938, *Special Report No. 22*, p. 219). He was also a Member of the Heterogeneity of Steel Ingots Committee and

of the Joint Sub-Committee on the Physical Chemistry of Steel-making, and was a Past-President of the Rotherham Technical Society.

Mr. Smith was a man of great personal charm and of unusual modesty. His outlook on life was rare in its unselfishness and he derived his greatest pleasure from the success of his juniors rather than from any personal achievement; he prided himself on building up an expert team among his staff and his dearest wish was to infuse the same spirit of cordiality and loyalty among the men at the works under his control. Progress in open-hearth steelmaking in Great Britain during the last decade owes as much to him as to any other man.

Mr. Smith joined the Institute in 1912.

CECIL EDWARD SQUIRE died suddenly on September 30th, 1942, at the age of sixty. Following his education at Christ's Hospital and the University College (now the University of Sheffield), where he gained a scholarship and numerous prizes and certificates, he was apprenticed to Messrs. Ambrose, Shardlow & Co., Ltd., Sheffield, general engineers. In 1902 he joined the staff of Messrs. Willford & Co., Ltd., manufacturers of all kinds of heavy laminated, helical and volute springs; he became successively personal assistant to the managing director in 1908, works manager in 1910, general manager in 1917 and joint managing director in 1926, and was managing director at the time of his death.

Mr. Squire was a leading authority on spring design and manufacture, and was the author of numerous papers on these subjects. He was a life member of the Institution of Mechanical Engineers and of the Sheffield Society of Engineers and Metallurgists, and a member of the Institution of Automobile Engineers, the Institution of Locomotive Engineers and the Junior Institution of Engineers (Chairman of the Sheffield Section in 1920-1921 and Vice-President in 1922-1923). He was an enthusiastic motorist, and built and rode his own motor cycle before 1906.

Mr. Squire became a Member of the Institute in 1930.

GEORGE STANFIELD died on November 20th, 1942. He had been associated for twenty-six years with the Brown-Firth Research Laboratories, Sheffield. In more recent years he contributed to the discussions on a number of papers on various metallurgical aspects presented to The Iron and Steel Institute, and was the author of two papers included in the First and Second Reports of the Alloy Steels Research Committee: "Temperature Distribution and Stress Effects in the Heating of Masses" (*Iron and Steel Institute*, 1936, *Special Report No. 14*) and "Quenching Tests in Various Media" (1939, *Special Report No. 24*). He was a Member of the Thermal Treatment and Special Aero-Components Sub-Committees of the Alloy Steels Research Committee and of the Stresses in

Moulds Panel of the Ingot Moulds Sub-Committee of the Committee on the Heterogeneity of Steel Ingots.

Mr. Stanfield was a member of the Institution of Mechanical Engineers, a Vice-President and Past-President of the Sheffield Metallurgical Association and a Member of Council of the Sheffield Society of Engineers and Metallurgists. He joined The Iron and Steel Institute in 1929.



## SECTION II.

# *A SURVEY OF LITERATURE ON THE MANUFACTURE AND PROPERTIES OF IRON AND STEEL, AND KINDRED SUBJECTS.*

## CONTENTS.

	PAGE
MINERAL RESOURCES . . . . .	1A, 87A
ORES—MINING AND TREATMENT . . . . .	2A, 41A, 88A, 131A, 194A
REFRACTORY MATERIALS . . . . .	3A, 42A, 89A, 131A, 162A, 195A
FUEL . . . . .	3A, 43A, 91A, 132A, 163A, 196A
PRODUCTION OF IRON . . . . .	7A, 45A, 94A, 133A, 166A, 198A
FOUNDRY PRACTICE . . . . .	8A, 47A, 95A, 134A, 167A, 200A
PRODUCTION OF STEEL . . . . .	11A, 50A, 103A, 137A, 169A, 203A
REHEATING FURNACES . . . . .	105A, 139A, 209A
FORGING, STAMPING AND DRAWING . . . . .	12A, 57A, 105A, 140A, 172A, 209A
ROLLING-MILL PRACTICE . . . . .	14A, 59A, 141A, 210A
PYROMETRY . . . . .	60A, 142A
HEAT TREATMENT . . . . .	16A, 61A, 106A, 143A, 173A, 211A
WELDING AND CUTTING . . . . .	19A, 65A, 108A, 144A, 174A, 214A
MACHINING . . . . .	22A, 111A
CLEANING AND PICKLING OF METALS . . . . .	22A, 112A, 175A
COATING OF METALS . . . . .	24A, 113A, 176A
PROPERTIES AND TESTS . . . . .	25A, 67A, 117A, 146A, 183A, 215A
METALLOGRAPHY AND CONSTITUTION . . . . .	34A, 74A, 124A, 152A, 186A, 221A
CORROSION OF IRON AND STEEL . . . . .	37A, 78A, 124A, 154A, 187A, 224A
ANALYSIS . . . . .	80A, 157A, 227A
BOOK NOTICES . . . . .	39A, 84A, 128A, 193A, 228A
BIBLIOGRAPHY . . . . .	84A, 159A, 230A

The Editor has been assisted in the preparation of this Survey by  
R. A. RONNEBECK.



## MINERAL RESOURCES

**Manganese Deposits in the Little Florida Mountains, Luna County, New Mexico.** S. G. Lasky. (United States Geological Survey, 1940, Bulletin 922-C).

**Chromite Deposits of Grant County, Oregon.** T. P. Thayer. (United States Geological Survey, 1940, Bulletin 922-D).

**Tungsten Deposits of Boulder County, Colorado.** T. S. Lovering. (United States Geological Survey, 1940, Bulletin 922-F).

**Manganese Deposits at Philipsburg Granite County, Montana.** E. N. Goddard. (United States Geological Survey, 1940, Bulletin 922-G).

**Tungsten Deposits of the Atolia District, San Bernardino and Kern Counties, California.** D. M. Lemmon and J. V. N. Dorr. (United States Geological Survey, 1940, Bulletin 922-H).

**Tin Deposits of the Black Range Catron and Sierra Counties, New Mexico.** C. Fries, jun. (United States Geological Survey, 1940, Bulletin 922-M).'

**Chromite Deposits of the Eastern Part of the Stillwater Complex, Stillwater County, Montana.** J. W. Peoples and A. L. Howland. (United States Geological Survey, 1940, Bulletin 922-N).

**Tungsten Deposits in the Tungsten Hills, Inyo County, California.** D. M. Lemmon. (United States Geological Survey, 1940, Bulletin 922-Q).

**Tungsten Deposits of the Benton Range, Mono County, California.** D. M. Lemmon. (United States Geological Survey, 1940, Bulletin 922-S).

**Some Structural Features of the Northern Anthracite Coal Basin, Pennsylvania.** N. H. Darton. (United States Geological Survey, 1940, Professional Paper 193-D).

**Domestic Manganese from Butte Helps in Emergency.** J. B. Hutt. (Engineering and Mining Journal, 1942, vol. 143, Jan., pp. 56-58). The author briefly describes the process of concentrating low-grade manganese ore from the Emma Mine, Butte, Montana. This ore contains about 21% of manganese and occurs chiefly as the mineral rhodochrosite in a siliceous gangue. Comparatively simple methods are used; the run-of-mine ore is concentrated to a flotation concentrate containing 38-40% of manganese, and this is nodulised in a rotary kiln and the carbon dioxide is removed. A flow-sheet for the plant is shown.

**Iron and Coal Resources of Japan.** (Vierteljahreshefte zur Statistik des Deutschen Reichs: Iron and Coal Trades Review, 1942, vol. 144, Apr. 10, p. 337). Some statistics are presented relating to the resources and production of coal and iron and manganese ores in Japan, Korea and Manchukuo as well as to the production of pig iron, ferro-alloys and steel for the years 1932 to 1936. The

principal iron ores are magnetite and hematite with an average of 50% of iron. It was estimated that in 1941 four million tons would be mined in Japan proper and a further two million tons would come from Korea.

## ORES—MINING AND TREATMENT

**Recent Developments in the Iron-Ore Industry and Blast-Furnace Practice.** T. L. Joseph. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 43-47, 58). The author reviews progress in the methods of mining, concentrating and smelting iron ores in the United States, especially Minnesota ores. Some companies are confronted with the rapid depletion of their reserves of higher-grade ore, with the result that the treatment of taconite is receiving attention; this ore contains 25-35% of iron, and it is at present uneconomic to concentrate it, but research on methods of concentrating it continues. The most promising application of flotation is in the treatment of washing plant tailings which contain about 20% of iron. This material has been accumulating at the rate of 5,000,000 tons a year and would require no grinding; laboratory tests have shown that such fines can be concentrated by flotation. The production of high-grade concentrates from New York and New Jersey magnetite has greatly expanded.

It has been demonstrated that hot metal for steelmaking containing only 0.70% of silicon can be produced, but not without some sacrifice in the sulphur content; this low-silicon iron requires much less limestone in the steel furnace and greatly reduces the amount of slag. A series of tests on the reduction of the silicon content of hot metal by adding mill-scale to the iron in the runner showed that 6.39 lb. of mill-scale to 100 lb. of iron at one particular works reduced the silicon from 0.96% to 0.49% and the manganese from 1.89% to 1.04%.

**Ore Bridges—Old and New.** G. F. Wolfe. (Iron and Steel Engineer, 1941, vol. 18, Dec., pp. 52-59). The author presents the results of a survey of a large number of bridges for handling iron ore at American iron and steel works and at docks. He discusses their design, maintenance and safety devices.

**Design and Operation of the Greenawalt Sintering Plant at the Julenhütte.** C. Schrupp. (Iron and Steel Institute, 1942, Translation Series, No. 76). An English translation of a paper which appeared in *Stahl und Eisen*, 1941, vol. 61, Aug. 21, pp. 785-791. (See Journ. I. and S.I., 1942, No. I., p. 43 A).

## REFRACTORY MATERIALS

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**Super Duty Fireclay Brick.** S. M. Swain. (American Refractories Institute : Industrial Heating, 1942, vol. 9, Jan., pp. 86-96). The author describes the manufacture and properties of super-duty fireclay bricks made at Cleveland, Ohio. Ground flint clay forms the basis of the mix, and small quantities of special materials such as calcined flint clay are added to control the shrinkage and density, or to improve the bond. The dry-press process is used for forming, and the pressure is held for a longer time than usual. The density of the pressed green brick is checked frequently. The important properties of these bricks are their high resistance to spalling over a wide temperature range and their resistance to slagging.

**Refractoria Quo Vadis.** J. D. Sullivan. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 72-75). The author reviews recent work in the United States on the improvement in the properties of refractory materials, and describes some of the minerals now being mined which are used in place of Austrian magnesite, Indian kyanite and the graphite which came from Ceylon and Madagascar.

**The Influence of Solids on the Decomposition of Carbon Monoxide and Methane.** W. Baukloh and J. Hellbrügge. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Oct., pp. 163-166). After reviewing the information available on the catalytic effect of metals and oxides in promoting the decomposition of carbon monoxide, the authors discuss the results of tests in which the influence of silica, burnt lime, alumina and chromic oxide when mixed with iron oxide on the decomposition of carbon monoxide was studied. Provided the temperature was high enough, these minerals retarded the decomposition, the chromium oxide being most effective in this respect. Mixing small amounts of zinc oxide, cadmium sulphate, mercuric chloride or boric acid with iron oxide had the same effect. Similar experiments with methane proved that this gas would also split up when heated in the presence of iron oxide. With both gases the decomposition causes the disintegration of the surrounding refractories, the action being more rapid with methane.

## FUEL

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**New Boilers at Algoma Steel Corporation, Ltd., Plant.** W. E. S. Dyer. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 146-149). The iron and steel works of the Algoma Steel Corporation, Ltd., at Sault Ste. Marie (see p. 11 A) had twenty-two boilers installed in four separate boiler-houses at considerable distances apart, but additions to the rolling-mill department increased the demand



for steam, and it was decided to erect a new boiler plant consisting of two 410-lb.-pressure units capable of producing 100,000 lb. of steam per hr. on blast-furnace gas, or 135,000 lb. per hr. on pulverised coal. A brief description of the plant is given in the present paper. The normal fuel is blast-furnace gas, but two of the three pulverisers are kept running idly, so that in the event of a failure in the gas supply, a practically instantaneous change-over to pulverised coal can be made.

**Modern Waste Heat Boiler Practice.** (Engineering and Boiler House Review, 1942, vol. 55, Apr., pp. 314–317). A number of types of waste-heat boiler for use at steelworks, gasworks and with exhaust gases from Diesel engines are described. Of particular interest is the use of shaped tubes in Cochran boilers. When gases are drawn through straight tubes they are not directed towards the tube walls, but by giving the tube a very slightly sinuous shape, the heat transmission can be accelerated 150% per unit of heating surface, because the gases are repeatedly directed against the tube walls.

**The Thermal Efficiency of Industrial Furnaces.** H. Schwiedessen. (Stahl und Eisen, 1942, vol. 62, Feb. 19, pp. 149–155). The author discusses the theory of heat transfer and the factors which make up the total heat given up by a stream of hot gas passing through a furnace. The following ratios and data are involved: (1) The heat given up by the gas to the heat of combustion; (2) the useful heat to the heat given up by the gas; and (3) the product of ratios (1) and (2) which equals the useful heat divided by the heat of combustion. The determination of these three ratios enables the thermal efficiency of furnaces of different design to be compared. The value of ratio (1) can be improved by (a) increasing the size and efficiency of the heat-absorbing surfaces, (b) making the furnace and flues air-tight, and (c) maintaining the gas-air mixture so that combustion takes place without any excess of either gas or air. A high value for the ratio of the useful heat to the heat given up in the furnace can be obtained by (a) having the furnace walls well insulated, and (b) increasing the ratio of the surface areas absorbing useful heat to the areas absorbing lost heat, *i.e.*, places such as flues where the heat absorbed is not used.

**What is Entropy and what Purpose does it Serve?** G. Neumann. (Stahl und Eisen, 1942, vol. 62, Jan. 29, pp. 89–91). The author states that first and foremost entropy is a mathematical expression which makes it possible to show in a single table the relation between the temperature, pressure, volume and heat content of a body in the temperature range from absolute zero to the highest temperatures attainable. He gives some examples of the application of entropy.

**The Coking Coals of Durham.** J. H. Jones. (Year-Book of the Coke Oven Managers' Association, 1942, pp. 106–121). The author summarises the nomenclature adopted in Durham for the lower coal seams which are of importance to the coking industry, and describes

the general change in character of the Durham coals in relation to the change in volatile matter throughout the coalfield. Large-scale experiments in another coalfield have shown that coke suitable for blast-furnace requirements can be made by blending 10–20% of first-class Durham coking coals with the local coals of lower caking power.

**Cleaning Coking Coals.** J. Griffen. (Eastern States and Chicago District Blast Furnace and Coke Oven Association: Steel, 1942, vol. 110, Mar. 2, pp. 80–83). The author quotes and discusses data which show the benefits obtained in the blast-furnace process in the Pittsburgh district by using coke produced from coal which has been mechanically cleaned.

**Repairing a Battery of Silica Ovens.** C. Dinsdale. (Year-Book of the Coke Oven Managers' Association, 1942, pp. 57–62). The author describes how extensive repairs were carried out to the brickwork of a battery of 40 regenerative vertical flue-ovens built in solid silica bricks from the regenerator walls. It was found advantageous to cool and heat up each oven consecutively whether it needed immediate repairs or not; thus as the work proceeded a progressive wave of descending and rising temperature from 1250° C. to 100° C. and back to 1250° C. passed along the battery, its lowest point being at the oven actually under repair. Six or seven ovens were idle at a time, the centre one of these being under repair. It was noted that the expansion of the untouched brickwork during the process was less than that of the new brickwork, and that, while the expansion of brickwork was taking place, the silica cement was still sufficiently plastic to permit any surplus to be squeezed from the joints.

**Difficulties of Modern By-Product Recovery.** T. B. Smith. (Year-Book of the Coke Oven Managers' Association, 1942, pp. 152–158). The author describes measures taken to counteract the deterioration in quality of some coke-oven by-products which has been caused by operating the ovens and other plant under war-time conditions. The measures described include: (1) The installation of a homogeniser and emulsifier for preparing an emulsion of light creosote oil, water and soft soap; this emulsion was added to the saturator to prevent the formation of black froth which badly discoloured the white ammonium sulphate crystals; and (2) increasing the capacity of settling tanks to deal with the increased content of free carbon in tar. Experiments with the object of decreasing the sulphur content of crude benzole are also described.

**Electrostatic Precipitation.** D. D. Howat. (Chemical Age, 1942, vol. 46, Mar. 28, pp. 165–168). The author explains the principles and advantages of the electrostatic precipitation process of cleaning gases. He describes how the process is applied for treating cement dusts, for removing dust from sulphur dioxide gases occurring in the roasting of zinc concentrates and for cleaning blast-furnace gas. Two combinations of treatment may be used for blast-furnace gas. In the first, the crude gas, passed

through a suitably packed cooling tower, is irrigated with a flow of water which reduces the temperature to  $25^{\circ}\text{C}$ . The dust and water vapour are then removed in a wet-type electrostatic precipitator. In the second method the temperature of the gas is reduced to  $80^{\circ}\text{C}$ . by passing it through an empty water-sprayed cooler; the greater part of the dust is then collected in a dry electrostatic cleaner. Finally, the gas is cooled to  $25^{\circ}\text{C}$ . by passage through a slate cooler, and small traces of dust, water-vapour and fog are removed in a wet-type electrostatic precipitator. Other applications dealt with more briefly are the cleaning of coke-oven gas, removing the last traces of acid mist, arsenic and chlorides from gases in contact sulphuric acid plants, recovering phosphoric acid in the reduction of phosphate ores and the recovery of fine suspensions of soda compounds in the waste gas from soda and kraft pulp mills.

**The Wet-Cleaning of Blast-Furnace Gas.** F. Thönnessen. (Stahl und Eisen, 1942, vol. 62, Jan. 22, pp. 61-65). The author reports on some experiments undertaken to improve the efficiency of the gas washers for cleaning blast-furnace gas at the Julienhütte. It was shown that the specified quantity of water for the Dingler washer could be reduced and the desired dust removal and cooling of the gas could still be maintained. This meant that the size and power requirements of the sludge plant could also be reduced. The beneficial effect of putting in a hot-water scrubber in front of the Dingler washer is discussed, and process data on water consumption and the reduction in the temperature and pressure of the gas at various stages of cleaning are presented.

**Dust Catchers for Gas Producers in Steelworks.** A. H. Leckie. (Iron and Steel, 1942, vol. 15, Feb., pp. 169-173; Mar., pp. 200-202). The conditions of steelworks producer-gas practice preclude the use of certain types of fine gas-cleaning plant, and dedusting is therefore carried out in simple types of settling chambers, or by cyclones, or a combination of both methods. The author outlines the fundamental principles of gravitation and of centrifugal separators and the theory of dust separation. Taking the case for a simple cyclone, he calculates its efficiency, and shows how the performance can be improved by certain modifications in design. Horizontal and vertical settling chambers and baffle-type catchers are briefly discussed and compared with the cyclone type. The possibilities of improving performance by connecting dust-catchers in series or parallel are examined, and it is concluded that there is probably little advantage in using cyclones in series or parallel. On the other hand, there is some advantage in placing horizontal settling chambers in series or parallel.

## PRODUCTION OF IRON

**Air Conditioning Improves Furnace Performance.** F. C. Wood. (Steel, 1942, vol. 110, Feb. 9, pp. 86-90). The author discusses the advantages gained by removing the moisture from blast-furnace blast down to 3 grains per cu. ft., and describes and illustrates a refrigeration dehumidifying plant for a blast-furnace producing 500 tons of iron per day.

**Correlations of Some Coke Properties with Blast-Furnace Operation.** H. W. Johnson. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1402: Metals Technology, 1941, vol. 8, Dec.). The author reports the results of several years' study of the factors affecting the properties of coke and how these properties affect blast-furnace operation. No concise specification for blast-furnace coke could be drawn up, as changes in a coke which resulted in an increase in the efficiency of one furnace caused a decrease in the efficiency of another. Data are presented and discussed on the following points: (1) Adapting an inefficient furnace to an available coke so that normal efficiency was restored; (2) the application of radial distribution of ore and coke to obtain the optimum contour of the layers when charging a blast-furnace; (3) the detrimental effect of a change in coke size on the production of a particular furnace; (4) limitations to the use of screen tests for coke as a measure of coke quality; and (5) the importance of the uniformity of the properties of coke for good blast-furnace operation.

**The Properties and Application of Foamed Blast-Furnace Slag.** L. Krüger. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Aug., pp. 63-74). The author reports on full-scale and laboratory tests of the weathering properties of bricks and light concrete made with foamed blast-furnace slag. Additional tests were also made to determine the behaviour of foamed slag in contact with mortars and with steel bars used for reinforcing. The properties of natural pumice and foamed slag are compared.

**The Hot-Refining of Cast Iron in Carbon-Monoxide/Carbon-Dioxide Mixtures.** W. Baukloh and U. Engelbert. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Nov., pp. 247-248). The authors report on some experiments relating to the "R.K." process of decarburising iron in which the effect of the temperature and of the CO/CO<sub>2</sub> ratio on the rate of decarburisation was examined. The "R.K." (Kalling-Rennerfelt) process has already been described (see Journ. I. and S.I., 1939, No. II., p. 137 p). Tests were made with grey and white cast iron containing carbon 3.6% and 3.35%, silicon 2.2% and 0.3%, and manganese 0.0% and 2.0% respectively. After 8 hr. treatment at 850° C. a ferritic boundary layer formed in the grey iron, which at higher temperatures became a hypereutectoid zone; although this was a layer with a low carbon matrix, graphite lamellæ remained in it and it required a long high-temperature



treatment to remove them. With a mixture of CO 82% and CO<sub>2</sub> 18% the white iron decarburised more rapidly than the grey. It was noted that the percentage decarburisation in a given time decreased linearly with increasing thickness of the specimen.

**Industrial Powder Metallurgy.** P. R. Kalischer. (Iron Age, 1942, vol. 149, Feb. 5, pp. 41-46; Feb. 12, pp. 46-51). The author explains the principles on which the manufacture of parts by the powder metallurgy process is based. To obtain a completely homogeneous material from metal powders in a time period which is not too long to be uneconomic the following conditions must be met: (1) The metals should be as chemically dissimilar as possible; (2) the crystalline structure of the metals should be similar; (3) their melting points should be as far apart as possible; and (4) the solid solubility of the metals in each other should be high. The process itself can be controlled by changing the shape, size and distribution of the particles, the forming pressure, the sintering temperature and the sintering time. A variety of articles made from ferrous and non-ferrous metal powders are described and die design and sintering atmospheres are discussed. The atmospheres used fall into two general classes—namely, those that prevent oxidation and reduce oxide films, and those which impart special properties to the powder compact. Pure hydrogen and dissociated ammonia with extremely low oxygen and moisture contents belong to the latter class. It has been found possible to harden parts made of iron powders by mixing a carburising gas with the hydrogen or other sintering atmosphere. If a mixture of iron powder, chromium powder and a very small amount of either titanium hydride or zirconium hydride is pressed and sintered at about 2012° F., sufficient nascent hydrogen is available from the hydride to reduce any chromium oxide and allow sintering to take place. The addition of a little titanium hydride has made possible the sintering of silicon.

**Terms Used in Powder Metallurgy.** (Metal Progress, 1942, vol. 41, Jan., pp. 44-46; Foundry Trade Journal, 1942, vol. 66, Apr. 2, p. 211). The Metals Handbook Committee of the American Society for Metals recently appointed a sub-committee to draw up a glossary of terms used in powder metallurgy. The glossary, containing about ninety definitions, is here reproduced.

## FOUNDRY PRACTICE

**Cupola Raw Materials.** G. O. Loach. (American Foundrymen's Association: Canadian Metals and Metallurgical Industries, 1942, vol. 5, Jan., pp. 6-9). The author discusses how cupola practice is affected by the war-time necessity of charging with a higher proportion of scrap and a lower proportion of pig iron. Methods of controlling the amounts of carbon, silicon, sulphur, manganese and



phosphorus in the melt are suggested, and the necessity of maintaining a constant level of bed coke, a uniform blast and of using additional limestone is pointed out.

**Converter Practice.** W. Hollinderbäumer. (Giesserei, 1941, vol. 28, Nov. 28, pp. 491-492). The author describes the melting and blowing practice at a steel foundry making thin-walled castings where a low-phosphorus iron is prepared in a cupola and desulphurised in the ladle. This iron is then put into a 3-ton converter for refining. Details of how the cupola charge is made up, slag removal, blowing and preparation of the converter lining are given.

**The Production of Moulding Sand Mixtures.** W. Reitmeister. (Giesserei, 1941, vol. 28, Oct. 31, pp. 445-449). The author has studied methods of specifying the properties of mixtures of moulding sands; for this purpose he explains how diagrams can be constructed which show how the porosity and strength of a mixture of two sands vary with the proportions by weight and by volume of fine- and coarse-grained sands in the mixture.

**New Methods in Mould Material Economy.** E. Knipp and G. Emde. (Giesserei, 1941, vol. 28, Nov. 28, pp. 481-491; Dec. 12, pp. 503-514). The authors report on an investigation of methods of treating used moulding sand from dumps which have hitherto been regarded as useless. After tests a satisfactory sand-washing machine was designed for treating the sand removed from castings. By blowing compressed air into the water, the water consumption was reduced from 15 to 3 cu. m. per ton of used sand, and 80% of the dust present was removed. Tests are described which show the detrimental effect on castings of too much dust in the sand. For steel castings there should not be more than 3% of dust (with grains up to 0.09 mm.) in the sand. A synthetic sand was prepared from the treated old sand. The pug-mill was the best type of mixer. For castings with walls 5-10 mm. thick the optimum milling time was 10-15 min., and 20-30 min. was best for castings 10-30 mm. thick. Generally speaking, the optimum clay content for green sand steel casting was 12-15%. If the mixture of washed used sand and clay was prepared with ample water to form a sludge which was then dried and put through the pug-mill, the resulting material had poor properties. The addition of binders such as dextrine and sulphite lye did not improve the properties, in fact the latter was detrimental; additions of graphite and coal dust had no effect. No beneficial effect for green sand casting could be attributed to raising the hygroscopicity of the clay by chemical treatment, but hydration of the clay by acid treatment had a beneficial effect on dry sand casting. The use of a binding clay of very coarse or very fine grain size was detrimental. Colloidal substances in the moulding sand increased the burning-on tendency and the number of defects. In general, the preparation of a synthetic sand from washed used sand and clay by the method described proved to be satisfactory and economic

for steel, grey iron, malleable iron, heavy metal and light metal castings.

**The Present Position of Core-Binders.** P. Tobias and G. Brinkmann. (Giesserei, 1941, vol. 28, Dec. 12, pp. 501-503). The authors report on an investigation of the composition and properties of five German core-binding compounds. Some of these were based on an emulsion of sulphite lye and pitch, and it was shown that the binding capacity depends mainly on the oxidation or polymerisation of the pitch and that increasing the proportion of pitch improves the binding power.

**Coremaking and Coredrying.** G. Hall. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 66, Apr. 9, p. 231). The author considers the preparation of core-sand mixtures for jobbing foundries. As a good mixture for green bonded oil sand cores he recommends the following: 68 lb. of sea-sand or the like, 7 lb. of Rayleigh sand,  $1\frac{1}{2}$  lb. of powder of the dextrine type and half a pint of linseed oil; this mixture should be milled for at least 10 min. in a paddle-mixer. Some information on core washes, drying-ovens and trolleys for carrying cores is also given.

**The Wet Process of Core Removal, Casting Cleaning, and Sand Reclamation.** R. Webster. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 66, Feb. 19, pp. 117-118). The author reviews the development of wet methods of cleaning the cores from castings. An early American method was to use jets of water at a pressure of 300-400 lb. per sq. in., which proved satisfactory for relatively soft and easily accessible cores. A German method was to use relatively small quantities of water at about 1200 lb. per sq. in. through a long nozzle projecting through the wall of the cleaning-room and operated from outside; this was not very successful owing to high maintenance costs for the pumps. The latest American process is that of wet-sand blasting. In this the machine sucks sand at a rather low velocity into a gun which ejects it at a velocity of about 20,000 ft. per min. This system has been previously described (*see* Journ. I. and S.I., 1941, No. II., p. 115 A).

**Casting Alloy Rolls.** P. R. Ramp. (Iron Age, 1942, vol. 149, Feb. 12, pp. 60-61). The author briefly describes a simple cope and drag mould with a split core for casting a hollow roll 11 ft. long, 13 in. outside dia. and 9 in. inside dia.

**Calculations Relating to Centrifugal Casting.** E. Diepschlag. (Giesserei, 1941, vol. 28, Nov. 14, pp. 465-469). When a revolving cylinder is partially filled with a liquid, as in the process of centrifugal casting, several forces act upon each particle of the liquid, and the resultant of these forces directly affects the movement of the liquid. In the present paper the author develops formulæ for determining the resultants for revolving cylindrical moulds in the horizontal, vertical and inclined positions.

## PRODUCTION OF STEEL

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**The Algoma Steel Corporation, Ltd.** C. Longenecker. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 112-135). The author presents a fully illustrated account of the history and present state of development of the iron and steel works of the Algoma Steel Corporation, Ltd., at Sault Ste. Marie, on the northern shore of the St. Mary's River in Ontario. The plant comprises, exclusive of the silica brickworks and ore mines: 158 coke-ovens, 4 blast-furnaces, 12 open-hearth furnaces, a Bessemer converter, 35-in. and 44-in. blooming mills, a 32-in. billet mill, a 30-in. rail and section mill, a 25-in. continuous billet mill, an 18-in. and a 12-in. merchant mill, sheet and tinplate mills and the necessary boiler-houses and engineering shops.

**Brazilian Steel Plant.** J. H. Drumm, jun. (Brazilian Business: British Steelmaker, 1942, vol. 8, May, pp. 92-93). A short account is given of the history of the erection of the iron and steel works of the Companhia Siderurgica Belgo-Mineira in the State of Minas Geraes, Brazil. (See Journ. I. and S.I., 1942, No. I., p. 224 A).

**Shell-Steel Manufacture.** C. M. Lichy. (Metal Progress, 1942, vol. 41, Jan., pp. 41-43). The author describes the melting, casting, soaking-pit and rolling-mill practice at an important American steelworks producing shell steel to the following analysis: carbon 0.30-0.50%, manganese 1.35-1.65%, phosphorus 0.050% max., sulphur 0.075-0.150% and silicon 0.15-0.30%.

**A New Method of Reversing for Open-Hearth Furnaces.** F. H. Schönwälder. (Stahl und Eisen, 1942, vol. 62, Jan. 8, pp. 30-32). The author describes the Reiner gas-reversing valve system for open-hearth furnaces. In this valve the plate to close the flue is made in two halves moving in housings on opposite sides of the passage. Each half is moved by a rack-and-pinion mechanism driven by a single electric motor. Considerable advantages have been observed due to the installation of these valves on two 35-ton furnaces fired by producer gas from brown coal briquettes; these include a reduction in the fuel consumption, a smaller temperature drop in the furnace during the reversing process, no foaming of the bath, more rapid melting and smoother furnace operation.

**Cost Analysis in Open-Hearth Steelworks. Part I. Determination and Preparation of Process Statistics.** K. Kudicke. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Oct., pp. 203-207).

**Cost Analysis in Open-Hearth Steelworks. Part II. Evaluation of Process Statistics in Process Book-Keeping.** L. Kopaja. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Nov., pp. 249-256).

**The Production of Steel in the Graphite Rod Resistor Furnace by the Remelting Process.** W. Geller and H. Hönig. (Stahl und Eisen, 1942, vol. 62, Jan. 1, pp. 9-14). The authors describe the designs of 2-cwt., 6-cwt. and 8-cwt. resistor furnaces for steelmaking, which

are heated by one or two horizontal graphite rods, and of a 1-ton furnace heated by three graphite rods. Operational data for a 2-cwt. and a 1-ton furnace at a German works making special steels are presented and discussed in detail. The economy of the 1-ton furnace is found to be practically equivalent to that of a coreless induction furnace. The horizontal cylindrical furnace proved to be more economical to work than the flat-hearth type. In general, experience has shown that electric furnaces of up to 1 ton capacity heated by graphite resistors form an efficient means of utilising electricity for the production of steel. The development possibilities of the process are discussed.

**Utilization of Stainless Scrap.** H. A. Grove. (Metal Progress, 1942, vol. 41, Jan., pp. 47-48). The author discusses the amount of stainless steel scrap available in the United States and factors relating to remelting it. It is estimated that of 250,000 tons of stainless-steel ingots produced in 1941, 87,000 tons became available at the steelworks for remelting. In addition, about 30,000 tons became scrap at works manufacturing finished articles, about half of which may find its way back to the steelworks. The total amount of scrap for remelting is therefore about 40% of the production. The amount of scrap which can be charged in the arc furnace depends on the desired amount of carbon in the stainless steel being made, but for low carbon grades the proportion of scrap must not exceed about 10%. There is thus a large surplus of scrap. It is hoped that the United States Government will modify some of their specifications and allow the carbon to be increased from 0.10% max. to 0.12% max., as this would enable a higher proportion of scrap to be charged.

**The High-Frequency Induction Furnace.** T. F. Wall. (Engineer, 1942, vol. 173, Mar. 6, pp. 209-211; Mar. 13, pp. 223-225; Mar. 20, pp. 242-243). In the first part of the paper the author explains the theory of the generation of heat by high-frequency currents, its application to steel furnaces and the stirring action of single-phase and polyphase currents. In the second part the principles of operation are explained and circuit diagrams are given.

## FORGING, STAMPING AND DRAWING

**"One-Shot" Method of Forging Shells.** W. P. Muir. (Iron Age, 1942, vol. 149, Feb. 26, pp. 43-46). The author gives an illustrated description of a new type of press for forging 4.5-in. shells from square billets. The billet is held in the vertical position in a split die, and the cavity is made in one downward movement of the piercer. The manner in which the billet is held and the piercer guide positioned immediately above the billet ensure the concentricity of the cavity. The novel feature of the machine is that the base of the die on which the end of the billet rests is not fixed, but



consists of a resistance pin resting on a hydraulic ram ; during the initial piercing the ram and pin remain stationary until the billet is fully expanded against the die walls ; the ram and pin then recede under controlled reduced pressure, thus permitting the nose of the shell to advance in front of the piercer.

**The Witter Shell-Forging Process.** J. H. Louix. (Mechanical Engineering, 1942, vol. 64, Feb., pp. 123-129). The author gives a detailed description, with many drawings and illustrations, of the Witter shell-forging process and the Assel cross-roll mill. (*See Journ. I. and S.I., 1941, No. I., p. 210 A*).

**Forging Buick Crankshafts.** A. F. Macconochie. (Steel, 1942, vol. 110, Mar. 2, pp. 66-68). A brief description with many illustrations is given of the method employed at an American automobile works for forging crankshafts. In the sequence of operations full advantage is taken of the original grain-flow of the rolled bar ; this is done by forging all the cranks in one plane and subsequently twisting the sections into their respective positions relative to the main axis.

**Important Factors in Forging Practice.** A. F. Macconochie. (Steel, 1942, vol. 110, Feb. 23, pp. 60-64). The author develops formulæ for making calculations relative to the flow of metal during forging operations.

**Spring Making.** C. W. Bartlett. (Steel, 1942, vol. 110, Feb. 16, pp. 85-88, 101 ; Feb. 23, pp. 66-71). A detailed and illustrated description is given of the presses and furnaces at an American works producing heavy leaf and helical springs for motor-cars and caterpillar tractors.

**Coining and Other Cold Press Work.** H. Chase. (Iron Age, 1942, vol. 149, Feb. 5, pp. 47-50). The author gives brief illustrated descriptions of unusual types of cold-pressing carried out by an American company. The examples include plugs with raised rims and square bosses, flanged hub-caps, split washers and semi-circular backings for small bearings.

**Use of Carbide Dies for Drawing Special Shapes.** J. R. Longwell. (Steel, 1942, vol. 110, Feb. 2, pp. 80-82). The author points out that when the quantity of specially shaped bars justifies the expense, it is now becoming a practice to make shaped cemented carbide dies for drawing bars, instead of machining them. To maintain maximum output it is essential to have a properly organised die stores and maintenance department.

**The Shape of Things to Come.** K. B. Lewis. (Mordica Memorial Lecture : Wire and Wire Products, 1942, vol. 17, Jan., pp. 15-27, 56-57). The author gives a comprehensive account of the history of the development of rolling rods and drawing wire.

**Mathematics for the Wire Mill.** D. Neuman. (Wire and Wire Products, 1941, vol. 16, June, pp. 329-331, 354). The author presents a number of formulæ which are useful for working out such data as percentage reduction in area of cross-section, percentage



elongation, percentage increase in tensile strength, feet per minute and pounds per hour production, and other factors which arise in wire rolling and drawing.

## ROLLING-MILL PRACTICE

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**The Theory of the Rolling Process between Unequally Driven Rolls.** E. Siebel. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Sept., pp. 125-128). The author expands his theory of the rolling process (see Journ. I. and S.I., 1925, No. II., p. 451) to include cases in which the rolls are unequally driven and do not transmit the same moment of rotation. The tangential forces acting in such cases and the factors affecting the position of the "neutral flow plane" are discussed. A method of calculating the position of the neutral flow planes and the roll slip when the equilibrium conditions prevailing in the space between rolls are known is given. The author's calculated results are in good agreement with those of Meurer (see Journ. I. and S.I., 1941, No. I., p. 212 A). *Note:* The German term *Fliessscheide* has been translated as "neutral flow plane," which is that position (plane) in the roll opening where the resistance to flow of the rolled material in the forward and in the backward direction is the same.

**Electrical Developments in the Steel Industry during 1941.** F. Mohler. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 55-58). The author describes some of the electrical machinery which has been installed in American rolling mills in 1941. The principal developments have been in connection with obtaining increased speeds in hot and cold strip mills and in obtaining more precise control of current supply.

**Developments in Rolling-Mill Electrical Equipment.** A. F. Kenyon. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 64-66, 75). The author gives particulars of new mill motors and motor-generator sets which have recently been put in at two 54-in. four-stand continuous strip mills at Cleveland, Ohio, at a new steel-works in course of construction at Houston, Texas, at a reconstructed continuous billet mill at Youngstown, and at a 140-in. plate-mill in the south.

**Centralized Steel-Mill Lubrication.** G. H. Kauffeld. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 59-63). The author describes the requirements of pressure-circulating lubrication systems for continuous strip-mills which operate from a central oil-pumping and purifying station. Separate pipe-line diagrams for the lubrication of mill motors, reduction gears, pinion stands and backing rolls are presented and discussed.

**The Röchling Rolling-Mill to the Broemel Patents. The Development of the Wide Strip Mill.** D. Timmermann. (Stahl und Eisen,

1942, vol. 62, Feb. 5, pp. 109-114). The principal characteristic of the Broemel patent for the rolling of wide strip is that one or more reheating furnaces, in which the strip is coiled, are inserted between the stands. A mill of this type has been erected at the Röchling steelworks at Völklingen, a description of which is given in the present paper. This mill consists of a three-high universal stand and two three-high finishing stands with the reheating furnace between them; it is planned to add two more stands and two furnaces. The furnace is rectangular in shape with a removable roof to facilitate repairs. It contains a friction-driven winding drum of a heat-resisting alloy. The strip from the second stand enters the furnace at one side below the drum, and is bent up on to the drum by a pressure roller and guide and coiled up. When the whole length has been wound up, the drum is rotated in the opposite direction, the strip leaving the furnace on the opposite side, whence it passes to the third stand. The furnace is gas-fired to a temperature of 800-900° C., and an even temperature is obtained throughout the length and breadth of the strip. The strip passes through the finishing stands at a speed of 3.5-4.5 m. per sec., and the mill described has given very satisfactory performance figures.

**Cold Rolling Steel Strip at 3900 Feet per Minute.** J. D. Campbell and J. R. Taylor. (Steel, 1942, vol. 110, Feb. 16, pp. 78-82, 115; Feb. 23, pp. 78-82). An illustrated description is given of a five-stand tandem cold mill installed in 1941 at the Irwin Works of the Carnegie-Illinois Steel Corporation. The stands are four-high and will roll strip up to 42 in. wide at coiling speeds on the tension reel of up to 3900 ft. per min. The main motor-generator set consists of a 12,000-h.p. synchronous motor, two 4000-kW. D.C. generators and a 60-kW. exciter for the synchronous motor.

**Influence of Forward Tension and Backward Tension in the Cold-Rolling of Strip Steel in a Twelve-High Cold-Rolling Mill.** W. Lueg and F. Schultze. (Iron and Steel Institute, 1942, Translation Series, No. 82). This is an English translation of a paper which appeared in *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1940, vol. 22, No. 7, pp. 93-108. (See Journ. I. and S.I., 1941, No. II., p. 173 A).

**Slitting—An Old Problem Modernized.** G. Kentis. (Iron and Steel Engineer, 1942, vol. 19, Feb., pp. 30-35). After a brief review of the history of slitting mills, the author describes and illustrates the characteristic features of modern slitting mills running at up to 1000 ft. per min. on light gauges.

**The Changing of Rolls.** D. Timmermann. (Stahl und Eisen, 1942, vol. 62, Jan. 15, pp. 41-48). The author discusses the problem of roll changing in heavy rolling-mills. Various methods and appliances for stands with different types of housings are described and illustrated; these include roll carriages and crane attachments. It is shown that for rapid roll changing it is necessary that not only the design of the stand, but also that of the roll trains and the general

layout of the mill must be given close attention from the very beginning.

**Special Electrical Applications in the Steel Industry.** J. D. Campbell. (Iron and Steel Engineer, 1942, vol. 19, Feb., pp. 78-89). The author describes a variety of electrical instruments of use in many stages of the manufacture of finished steel, but mainly in the rolling-mill. The instruments include thickness gauges for both magnetic and non-magnetic materials, a strain-gauge, pressure-gauges for measuring the mechanical pressure applied to cutting tools and the pressure between the electrodes of resistance welding machines, a photo-electric width-gauge for moving strip, electric control for strip-polishing belts, amplidyne control for synchronising the speed of flying shears to that of the strip to be cut, and controls for reversing-mills and looping-mills.

## HEAT TREATMENT

**The Selection of Steels for Carburising.** I. Stewart. (Iron and Steel, 1942, vol. 15, Feb., pp. 191-194). In discussing the selection of steels for case-hardening, with special reference to gear manufacture, the author refers to the present tendency to use steels of higher carbon content than formerly. The relationship between case depth and core strength, the manner in which grain size affects machinability, distortion during heat treatment and the physical properties of hardened parts, and the hardening characteristics of carbon steels and of nickel-chromium-molybdenum steels are dealt with.

**Molybdenum High Speed Steels and their Heat Treatment.** L. C. Grimshaw and R. P. Kells. (Metal Progress, 1942, vol. 41, Jan., pp. 76-81). After pointing out that the use of molybdenum steels low in tungsten for high-speed machining is by no means new, the authors discuss methods of heat-treating them. Six types of steel containing up to 9% of molybdenum, up to 6% of tungsten, up to 3.20% of vanadium, 3.75-4.25% of chromium and carbon up to 1.20% are considered. These steels decarburise more easily than the 18/4/1 type and are all more susceptible to grain-growth. If a semi-muffle furnace without a protective atmosphere is used for heat-treating molybdenum steel tools, they should first be dipped into a saturated solution of borax in water that is heated to 150-180° F. If this solution is made with boric acid flakes instead of borax, the residue on the surface after heat treatment will not be hard and glossy. If a tool of 18/4/1 steel is overheated by 75° F. it will still make a satisfactory tool, but the hardening temperature of the molybdenum steels is 100-150° F. lower than for 18/4/1 steel, and very little overheating is permissible; efficient temperature control of the furnace is therefore essential. Details of the hardening

and tempering temperatures and of the grain size obtained are given for the six analyses of steel.

**Obtains Improved Performance with Salt Bath Furnaces.** (Steel, 1942, vol. 110, Mar. 2, pp. 98-101). An illustrated description is given of a salt-bath heat-treatment unit with a bath 10 ft. long  $\times$  2 ft. wide, through which the charge passes while suspended from a rail. The conveyor carries a large number of small parts on a wire rack, and this is automatically lowered down the inclined rail to enter the bath, moved slowly along the horizontal portion and hoisted up the incline at the exit end.

**Special Phenomena in Connection with the Scaling of Heat-Resistant Steels and Alloys.** G. Bandel. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Dec., pp. 271-283). The author points out that two fundamentally different types of scale may be formed on heat-resistant steels, *viz.*, (a) scale consisting of the oxide of the effective alloy component, *i.e.*, that which is most liable to oxide formation, and (b) scale consisting of iron oxides. Occasionally both types of scale are found on the same specimen. A layer of the former type forms an effective protection against further scaling, whereas a layer of the latter has little protective value at temperatures above 550° C., owing to the great permeability of iron oxides to oxygen at higher temperatures. The author discusses the conditions which lead to the formation of the two types of scale. He points out that a protective layer of scale can be formed only if there is a primary layer with high iron oxide content above it, and that its formation is greatly affected by the alloy composition, the temperature and the surrounding medium, and further, that the presence of mill-scale and casting skins may interfere with its development. He then discusses numerous causes which may lead to the destruction of a protective scale layer, especially the secondary local formation of scale rich in iron oxides, the scaling loss at edges and corners, external mechanical and chemical effects, the presence of inclusions in the material and the oxidation of certain alloy components (boron, vanadium, tungsten and molybdenum). A special paragraph is devoted to the local scale formation of chromium-nickel steels exposed to sulphur-containing gases, and it is shown that the attack is particularly severe if crusts, *e.g.*, of lime, are formed on the steel, as sulphur will be accumulated in these and act in the form of sulphide. Finally the relation is discussed between the orientations of the crystals of the steel and those of the scale. The paper is illustrated by numerous photographs representing unusual cases of scale formation.

**The Scaling of Steels Alloyed with Vanadium.** H. Cornelius and W. Bungardt. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Aug., pp. 107-113). The authors report the results of tests on the influence of additions of up to 4.70% of vanadium to plain and alloy steels on the scale formation at different temperatures. At temperatures up to 900° C. the addition of vanadium slightly increased



the scaling resistance of unalloyed steels; at higher temperatures the vanadium had no effect. It is probable that below 900° C. the scale containing vanadium oxide is denser than the scale of the vanadium-free iron. Between 0.5% and 2.0% of vanadium had practically no effect on the scaling resistance of steels containing chromium, chromium and silicon, chromium and manganese, and chromium and nickel (not too high in nickel) at temperatures at which these steels normally have a good resistance to scaling. At higher temperatures 2% of vanadium increased the scaling resistance of all these steels. The scaling of chromium-nickel steels high in nickel was only slightly changed by adding 0.5% of vanadium, whilst 2% of vanadium markedly decreased their scaling resistance. The time taken for the normal initial scaling of a chromium-nickel steel decreased with increasing nickel content, and after this there was a rapid increase in the scale formation; this also occurs with iron-aluminium alloys. The amount by which vanadium additions increased the scaling of the steels high in nickel on annealing in the products of combustion of town gas was much less than when the specimens were heated in air. A metallographic investigation was made of the effects of the scaling on the steel-scale interface.

**The Influence of Vanadium on the Scaling of Steel.** (Metallurgist, 1941, vol. 13, Oct., pp. 35-36). Reference is made to some recent German technical articles on the effect of vanadium on the scaling of alloy steels, and much of the information in a paper by Cornelius and Bungardt in which they give the results of many of their own experiments is quoted. (See preceding abstract).

**Recent Developments in Electric Furnaces for Heat Treating.** C. L. Ipsen. (Industrial Heating, 1942, vol. 9, Jan., pp. 48-54). The author describes some small rectangular electric furnaces for use with protective atmospheres for heat-treating small parts and pusher electric furnaces for heat-treating shells.

**Furnaces for Armament. Part VI. Furnaces for Nosing and Heat Treatment of Bombs.** (Industrial Heating, 1941, vol. 8, Dec., pp. 1365-1368, 1390). Brief descriptions are given of furnaces for heating steel bomb casings. The types described include: (a) An oil-fired furnace for heating the ends of steel tubes from 10 to 14 in. in dia. so that these can be closed by forging to form the nose of the bomb; (b) a radiant-roof furnace for annealing forged alloy steel bombs and gas cylinders; (c) a hardening furnace; and (d) a continuous furnace for tempering.

**Heat Treating Cold-Headed Products.** H. Chase. (Steel, 1942, vol. 110, Mar. 2, pp. 72-74). The author describes some gas-fired and electric furnaces for the heat treatment of small parts such as bolts and nuts made by cold-heading.

**Direct-Fired Catenary Furnace.** (Steel, 1942, vol. 110, Feb. 16, pp. 96-98). A description is given of a continuous gas-fired furnace for annealing stainless steel strip up to 10 in. wide. The furnace is heated by fourteen burners on each side, some positioned above the



strip and others below it. The strip hangs in a shallow curve as it passes through the furnace. Complete combustion is controlled by the gas-air proportioning valves and there is no muffle.

**The Appropriate Hardening of Chromium-Manganese Case-Hardening Steels after Carburising.** J. Kreim. (Stahl und Eisen, 1942, vol. 62, Feb. 12, pp. 130-136). The author reports on an investigation of suitable hardening treatments for carburised steels containing carbon 0.15-0.20%, manganese 1.2-1.5% and chromium 0.8-1.5%. Data are presented to show how the time and temperature of the carburising treatment and the temperature of the subsequent hardening treatment affected the physical properties and the structure of the case and core. It was established that a single subsequent hardening treatment at not exceeding 820-830° C. could be employed with advantage for case depths up to 1 mm. With a thicker case the part should not be cooled too slowly in the carburising treatment. For parts of considerable thickness with a deep case a double tempering treatment is generally necessary.

**Methods for the Quenching of Steel. Part III.** M. H. Mawhinney. (Industrial Heating, 1942, vol. 9, Jan., pp. 26-28). Continuation of a series of articles (*see* Journ. I. and S.I., 1941, No. II., p. 12 A). The author describes and illustrates various types of cradles and baskets used for quenching bars and small parts in batches.

## WELDING AND CUTTING

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**The Weldability of Steels.** W. H. Bruckner. (Welding Journal, 1942, vol. 21, Jan., pp. 55-S-59-S). The author considers various tests for determining the weldability of steel, and reports the results of hardness tests and determinations of the cooling rate in the heat-affected zone of specimens of fifteen low-alloy steels containing nickel and copper, using the weld-quench procedure described in an earlier paper (*see* Journ. I. and S.I., 1938, No. II., p. 160 A).

**The Tee-Bend Test to Compare the Welding Quality of Steels.** G. A. Ellinger, A. G. Bissell and M. L. Williams. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Jan., pp. 1-49). The authors describe a weldability test for steel in which specimens of double-fillet welded T section are prepared and bent in a special jig. The results obtained with eighteen low-alloy high-tensile steels at temperatures from 70° F. down to -20° F. are given. The criteria used for comparison were the maximum load, the angle at maximum load and the type and location of the fractures. A special method of statistical analysis was used to evaluate the data and compare the weldability; this method is described in detail.

**An Analysis of the Bend Test on Weld Metal.** O. Werner. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Nov., pp. 219-229). The bend test in which a single bead of weld metal deposited on a thick plate is bent with the bend in tension has been previously described and discussed (*see* Journ. I. and S.I., 1938, No. II., p. 23 A). In the present paper the author reports on an investigation of the correlations between the different data obtained with this test when the bead was deposited on a 40-mm.-thick plate of a copper-bearing low-chromium steel. It was established that the angle to which the specimen could be bent before fracture could be more or less related to several of the properties of the steel. By means of dilatometric measurements it was possible to determine the hysteresis loop for the  $A_1$  transformation, and from this, in conjunction with hardness data, to determine the tendency to the local formation of martensite and to the development of transformation stresses. The tendency to form martensite was particularly noticeable in the coarse-grained  $\gamma$  steels. Compared with that of the material the method of welding had little influence on the properties of the weld. As the angle at fracture in the bend test decreased the number of micro-cracks in the material increased. It appears that the plastic range in the heat-affected zone of this steel is very small. Experience obtained with spring steels leads to the belief that not only does fine-grained notch-sensitive steel give good results in the bend test on weld metal, but so also does a banded secondary structure in a not quite so finely grained steel. The relation between the notched-bar impact strength of specimens cut in and across the direction of rolling as an indication of the tendency of a specimen to fracture without deformation in the bend test on weld metal was also studied.

**The Effect of the Composition on the Properties of Welded Facings.** H. Cornelius. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, July, pp. 47-58). The author reports on an investigation of the structure, stability, degree of scaling, hardness and sensitivity to cracking at high temperatures of twenty-seven different alloys with compositions within the following limits: carbon 1.1-4.2%, manganese 0.2-6.8%, chromium 23-29%, cobalt 0-65%, tungsten 0-16%, molybdenum 0-4.6% and vanadium 0-3.1%. The results are presented by tables, curves and micrographs. Recommendations are made as to the composition of those alloys with reduced percentages of expensive imported elements (particularly cobalt and tungsten) which are substitutes for stellite and are suitable for the welded facings to make exhaust valve faces and seats for aero engines.

**Metallographic Investigations and Bending Fatigue Tests on Thin Welded Plates of High Tensile Steel.** R. Mailänder, W. Szubinski and H. J. Wiester. (Technische Mitteilungen Krupp: Welding Journal, 1942, vol. 21, Jan., pp. 30-S-33-S). To determine the weldability of thin high-tensile steel as used for sheets and tubes in the aircraft industry, the authors studied the metallographic struc-

ture, hardness and bending fatigue strength of a carbon steel, three manganese steels and three chromium-molybdenum steels. The tests were made on unwelded, atomic-hydrogen welded and acetylene welded specimens. The following conclusions were reached: (1) Although generally for unwelded metals the endurance limit increases with increasing tensile strength, this did not apply for welded specimens in the tensile strength range of 76,800–114,000 lb. per sq. in. (2) The endurance limit increased with decreasing thickness. (3) The endurance limit of welded chromium-molybdenum steel sheet about 1.8 mm. thick used for aircraft is about 31,000–36,000 lb. per sq. in.; the special manganese steels tested were equal in strength to the former steels and were less sensitive to welding cracks. (4) The fatigue strengths of atomic hydrogen welded and acetylene welded steel were about the same. (5) Machining after welding increased the fatigue strength considerably. (6) The rate of cooling of the heat-affected zones was very close to the critical cooling rate of all the steels tested; all possible devices must therefore be used to decrease the rate of cooling of welded assemblies. (7) A low carbon content keeps the hardening capacity of the low alloy steels within moderate limits.

**Notch Sensitivity of Welds under Repeated Loading.** H. L. Daasch. (Welding Journal, 1942, vol. 21, Jan., pp. 60-S–64-S). The author reports the results of tests to determine the effect of notches on the fatigue strength of specimens of welded 0.25% carbon steel. The ratio of the endurance limit to the tensile strength was 0.45. The notch-sensitivity ratio in fatigue, which is the ratio of the endurance limit of unnotched specimens to that of notched specimens, was 1.34 with a notch of radius  $\frac{1}{8}$  in., and 1.80 for a 90° sharp V notch.

**Investigations of the Occurrence of Cracks in Welded Bridges.** H. Busch and W. Reulecke. (Stahl und Eisen, 1942, vol. 62, Jan. 22, pp. 66–72). The authors report on tests on specimens of steel from the welded bridge at Hasselt, Belgium, which broke in March 1938. The chemical composition, hardness, elastic limit, tensile strength, reduction of area, notched-bar impact strength, ageing tendency and welding properties were all studied. The bridge was built of rimming basic-Bessemer steel with a tensile strength of 40–45 kg. per sq. mm. and welded with coated electrodes. The original fractures occurred without deformation at an atmospheric temperature of  $-20^{\circ}\text{C}$ . From the test data it was thought that the failure of the structure was probably due to: (1) Bad design of the welded joints which caused multi-axial welding stresses; (2) the very low temperature of the atmosphere; and (3) the low notched-bar impact strength of the steel at  $-20^{\circ}\text{C}$ .

**Oxy-acetylene Machine Cutting Speeds Upped 20 to 30 per Cent.** A. H. Yoch. (Steel, 1942, vol. 110, Feb. 16, pp. 93–94). The author describes a new design of burner nozzle for oxy-acetylene machine cutting with which a higher cutting speed can be obtained without

any increase in the oxygen consumption. This advantage has been obtained by providing a slightly expanding orifice from which the cutting oxygen flows. This permits some expansion of oxygen to take place before it leaves the burner, and reduces the turbulence in the air between the nozzle and the work. The gap left by the flame in the steel is narrower than with the ordinary burners.

## MACHINING

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**Drilling Hardened Parts.** L. G. Black. (Iron Age, 1942, vol. 149, Feb. 26, pp. 54-56). Some information is given on the use of "Hardsteel" drills for particularly arduous service. The composition of the steel is not stated. The drills are triangular in section and are revolved at a higher speed than that for drilling mild steel with high-speed steel drills. It is claimed that hardened dies, files and manganese steels can be drilled without difficulty with Hardsteel.

**Cemented Carbide Tools.** (Automobile Engineer, 1942, vol. 32, Mar., pp. 91-94). Details are given of the most recent available information concerning the treatment and application of cemented carbide tools in Germany. Methods of preparing the tips and fixing them to the shank are described, as well as the methods of grinding necessary to ensure optimum results. Tool angles are fully discussed and limiting values for these angles for machining a wide range of materials are presented in tabular form. The cutting speeds for rough- and finish-machining of all materials commonly machined with carbide-tipped tools are given.

**Performance of Cutting Tools.** L. J. St. Clair. (Iron and Steel Engineer, 1941, vol. 18, Dec., pp. 61-63). The author considers the characteristics of the following types of cutting tools: (1) Diamond tools; (2) carbon steel tools; (3) 18/4/1 (tungsten-chromium-vanadium) high-speed steel tools; (4) cobalt high-speed steel tools; (5) carbide tools; and (6) cobalt-chromium-tungsten cast tools. He gives some examples of machining problems and gives reasons why a particular type of tool is applicable to each.

## CLEANING AND PICKLING OF METALS

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**The Oxygen-Scarfig of Steel.** L. Wolff. (Stahl und Eisen, 1941, vol. 61, Dec. 11, pp. 1126-1134). Similar appliances are used for the oxygen or flame-scarfig of steel billets as for oxy-acetylene cutting. The author reports on investigations of the effects of different-shaped burner nozzles and of oxygen and acetylene pressure and consumption on the smoothness, hardness and structure of the



flame-scarfed surface of steel. The structure at the surface depends on the rate of cooling, which may be as high as  $600^{\circ}\text{C}$ . per sec., depending on the carbon content, billet dimensions and rate of travel of the burner. The flame causes neither carburisation nor decarburisation of the surface, and below 1.5 mm. from the surface there is no change in the structure. High-carbon steels and steels alloyed with elements which lower the critical cooling rate should be preheated to about  $200^{\circ}\text{C}$ . before flame-scarfing. Special high-alloy steels cannot be flame-scarfed. The process costs much less than square-turning, grinding or chipping with pneumatic tools.

**Tests Show Effectiveness of Flame-Cleaning Structural Steel.** E. A. Tice. (Steel, 1942, vol. 110, Feb. 9, pp. 64-68). The author reports the results of some tests at an American steelworks in which cleaning with an oxy-acetylene burner is compared with wire-brushing as a means of preparing steel for painting. In the case of rusty steel the paint had a very much longer life after cleaning with a burner than after brushing, but with new steel there was little to choose between the two methods.

**Autogenous Deseaming for Removing Surface Defects from Ingots and Blooms.** J. Averstén. (Iron and Steel Institute, 1942, Translation Series, No. 84). This is an English translation of a paper which appeared in *Jernkontorets Annaler*, 1940, vol. 124, No. 5, pp. 212-224. (See *Journ. I. and S.I.*, 1941, No. I., p. 19 A).

**Investigation of the Economy of a Bloom Planing Machine Compared with Bloom Cleaning with a Pneumatic Chisel.** H. Rübmann. (Stahl und Eisen, 1942, vol. 62, Feb. 19, pp. 160-164). The author gives a detailed and illustrated description of a hydraulic planing machine for cleaning the surface of blooms. The bed of the machine can be tilted to  $45^{\circ}$ , and it has two pairs of jaws to grip the bloom. The planing is done with the face of the bloom at  $45^{\circ}$  to the horizontal, so that the operator has a good view to control the work. The to-and-fro movement of the table is controlled by foot pedals, and the chisel movements by switches operated by hand. The machine-head carries two heavy clamps, each of which takes a gouging chisel and a flat planing tool. Blooms up to 350 mm. square and 4.5 m. long can be planed. The results of a time study of the planing process are given and the data are compared with the time required and the output achieved with the hand-operated pneumatic chisel, the comparison revealing the very great advantages arising from the installation of the machine.

**Cathodic Pickling in the Presence of Inhibitors.** W. Machu and O. Ungersböck. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Jan., pp. 301-306). The authors describe an electrolytic method for the pickling of iron and steel articles in hydrochloric or sulphuric acid in the presence of organic inhibitors. The quantity of the latter which is required is only a tenth to a twentieth part of that added when pickling without the application of an electric current. On the other hand, the current density required is only one-hundredth to



one-thousandth of that necessary in the absence of inhibitors. The intensity of pickling can easily be regulated by modification of the current density. The quantity of hydrogen adsorbed by the articles treated is smaller than in standard pickling methods, so that it is given off easily. The surfaces obtained are uniformly smooth and bright and free from pitting.

## COATING OF METALS

**Rectifiers in Hard Chrome Plating.** J. C. Bogle. (Iron Age, 1942, vol. 149, Feb. 5, pp. 56-58). The author describes some examples of the application of current rectifiers in place of motor-generator sets for supplying current to tanks for hard-chromium plating.

**The Technique of Heavy Nickel Plating.** W. M. Tucker. (Monthly Review of the American Electroplaters' Society, 1942, Mar., pp. 196-210). The author describes some nickel-plating experiments using a modification of Watt's bath in which the effect of variations in the nickel, chloride and boric acid contents was studied. The following conclusions were arrived at: (1) The nickel content of the Watt's type of solution was relatively unimportant; (2) higher current densities could be used with higher nickel contents; (3) changes in the sulphate ion had no significant effect; (4) increasing the chloride ion increased the hardness and decreased the crystal size of the deposit; and (5) the boric acid content was not critical, but increasing this reduced the crystal size of the deposit.

**Lead Plating.** A. G. Gray and W. Blum. (Electrochemical Society, 1941, Oct., Paper No. 80-39). Detailed descriptions are given of the procedure for the electrodeposition of lead using fluosilicate and fluoborate baths. Instructions are also given for testing the lead coating produced.

**Hot Galvanizing.** A. T. Baldwin. (Iron Age, 1942, vol. 149, Jan. 22, pp. 44-47). The author discusses factors affecting the quality of zinc coatings obtained by the hot-dip process and the amount of dross, ashes and skimmings formed in relation to the amount of zinc used. It is shown that as the immersion time is increased the thickness of the iron-zinc alloy layer increases, whilst the adherence and ductility of the coating decrease.

**Electrolytic Tinplate.** M. D. Stone. (Iron and Steel Engineer, 1942, vol. 19, Feb., pp. 90-96). The author discusses the problem of designing a continuous electrolytic tinning plant capable of tinning cold-rolled, annealed and temper-passed low-carbon steel strip with a coating weighing  $\frac{1}{2}$  lb. per base box, at 500 ft. per min., the strip being 0.007-0.011 in. thick, 16-38 in. wide in coil lengths of 5000-10,000 ft. weighing 5 to 11 tons per coil. Some of the data obtained in the running of a pilot plant are given, and the sequence

of processes in the full-scale plant, which is now in successful operation, is described.

**Recovers Base Metal from Old Tin Cans.** (Diesel Power : Steel, 1942, vol. 110, Jan. 19, pp. 76-77). A brief description is given of a small detinning plant producing about 2 tons of compressed detinned scrap in an 8-hr. day. The tin and dirt are burnt off the cans in an oil-fired rotating drum maintained at about 900° F., after which the clean cans pass down a chute to a hammer mill driven by a 50-h.p. Diesel engine.

## PROPERTIES AND TESTS

**Rapid Tension Tests Using the Two-Load Method.** A. V. de Forest, C. W. MacGregor and A. R. Anderson. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1393 : Metals Technology, 1941, vol. 8, Dec.). The authors report on experiments made to determine how the speed of testing affected the true stress-strain characteristics of three steels and one brass. Both slow static tension tests and low-velocity Izod impact-tension tests were conducted in the manner previously described by MacGregor (*see* Journ. I. and S.I., 1940, No. I., p. 295 A). The steel specimens were of the S.A.E. 1112, 1045 and 3140 types. In all cases the true stresses corresponding to the maximum load increased by from 6.9% to 14.9% when tested by the low-velocity impact technique as compared with the values in static tension; the true stress at fracture increased by from 11.3% to 40.6%, and with the exception of steel S.A.E. 1112, the true strain at fracture increased by from 3.1% to 23.3%.

**The Notched-Bar Bend Test.** H. Hauttmann. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Jan., pp. 331-338). The author developed a bend test for the examination of specimens in which a zone of local embrittlement on the side in tension is produced by a longitudinal cold-pressed groove. The test thus serves the same purpose as the bend test on weld metal, but has the advantage of being more easily reproduced. It can be applied to the examination of specimens in the aged as well as in the non-aged state. The groove is normally semi-circular, 5 mm. in dia. and 150-250 mm. long. The testing conditions can be modified, however, by varying the shape of the groove and, further, by making a 45° notch of 1 mm. depth across it. The author reports on numerous results which he obtained with the new test in the examination of killed and rimming basic Bessemer steel, of boiler plate, and of ordinary and special qualities of steel St 52, and compares the results with those of bend tests on weld metal and notched-bar impact tests.

**Theory of Lattice Expansion Introduced by Cold-Work.** C. Zener. (American Institute of Mining and Metallurgical Engineers, Technical

Publication No. 1403: Metals Technology, 1941, vol. 8, Dec.). The author considers two theories which offer explanations for the fact that cold-working a metal causes a decrease in its density with an increase in its volume. One is that the increased number of crystallites randomly orientated causes the expansion, and the other is that the cold-work distorts the grains and that this leads to an increase in volume. He rejects the former and accepts the latter. It is found that the volume of a metal with no external forces acting on it is greater when internal stresses are present than when they are absent, and the increase in volume is proportional to the energy associated with these internal stresses. From a quantitative calculation the author shows that the expansion is of the right order of magnitude to account for the observed decrease in density of metals when cold-worked.

**Crystal Structure in Steel and the Effect of Hot and Cold Work.**

A. F. Macconochie. (Steel, 1942, vol. 110, Feb. 16, pp. 66-70, 114). The author explains what is meant by face-centred and body-centred cubic lattice structures and discusses the effects of hot and cold work on steel. In cold work the grains are elongated in the direction of working, giving rise to a fibre-like structure and raising the tensile strength and elastic limit, the metal becoming increasingly brittle. In hot work the grains are also deformed, but the strain produced is not permanent, other factors such as non-metallic inclusions affecting the final structure.

**Structure and Properties of Forgings.** G. W. Birdsall. (Steel, 1942, vol. 110, Feb. 9, pp. 57-62, 68). In a series of questions followed by explanatory answers rather than definitions the author points out the characteristics of forgings, especially those relating to inclusions, crystal growth, grain-flow, effects of hot working and the directional properties.

**The Strength Properties of Molybdenum-Free Case-Hardening and Heat-Treatable Steels.** A. Krisch. (Stahl und Eisen, 1942, vol. 12, Jan. 8, pp. 48-53). An abridged version of the paper by Pomp and Krisch which appeared in *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1941, vol. 23, No. 10, pp. 135-185 is presented. (See *Journ. I. and S.I.*, 1942, No. I., p. 210 A).

**Influence of the Testing Conditions on Wear Tests by Spindel's Method.** H. Esser and H. Arend. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Aug., pp. 103-106). The authors present the results of wear tests by Spindel's testing technique (see *Journ. I. and S.I.*, 1926, No. II., p. 636) which show the effects of variations in the pressure and speed of the rubbing surfaces and the width of the face of the revolving disc. The tests were carried out on three normalised steels containing 0.30%, 0.60% and 0.75% of carbon respectively. It was established that, when using wide-faced discs, there was a critical rate of wear at which this rate was independent of the pressure applied.

**Machinability of Metals.** D. O. Morris. (Australian Institute of Metals: Australasian Engineer, 1942, vol. 42, Jan. 7, pp. 10-12, 36-37). In this study of machinability the author distinguishes between three types of chips, *i.e.*, discontinuous chips, and continuous chips with and without built-up edges. The first is usually indicative of low power consumption and reasonable tool life, the second indicates a very good finish with reasonably low power consumption, and the third is usually characterised by a poor finish with a good tool life. The properties of the metal and of the tool which are associated with these characteristics and the effects of carbon, manganese, phosphorus, sulphur, silicon and some alloying elements on the machinability of steels are pointed out. Finally, different machining operations, the properties of cutting fluids and machinability tests are discussed.

**Interpretation of Trials on Tool Steels.** B. Thomas. (Metallurgia, 1942, vol. 25, Mar., pp. 133-134). The author gives two examples of methods of calculating the cost and life of tool steels which demonstrate how these two factors can be correctly related. The first example relates to the selection of one from five steels for shear-blades, and the second to the substitution of a tungsten steel at 3s. per lb. for a high carbon steel at  $1\frac{3}{4}d.$  per lb. for a die for a hot-drifting operation on thousands of small parts.

**Cold-Deformed Manganese Steel as a New Material for Magnets.** W. Jellinghaus. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Aug., pp. 99-101). The author discusses the magnetic properties of low carbon iron-manganese alloys containing 13-15% of manganese. Cold-rolling converts some of the austenite of this alloy to martensite, but if this cold-deformed alloy is tempered at 500-575° C. some of this martensite is transformed back to austenite. In this partial transformation a migration of the manganese takes place from the martensite to the austenite, the manganese in the former being reduced to about 5% below the average manganese content of the steel. This movement of the manganese lowers the magnetic saturation and remanence and increases the coercive force. Manganese steels treated in this way are suitable for making thin steel sheets for magnets.

**The Influence of Temperature on Creep Strength.** H. Esser and H. Schmitz. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, July, pp. 19-25). This investigation is a continuation of the creep strength investigations reported previously by Esser and Eckardt (*see* Journ. I. and S.I., 1940, No. I., p. 99 A). The results of short-time creep tests on two low carbon steels and two chromium-molybdenum steels at temperatures in the 300-600° C. range are reported. The straight-line relationship obtained at lower temperatures, when plotting the load against the creep rate using logarithmic scales, only applies for high temperatures during the first stages of the test; the test in 10-hr. stages can therefore be used to determine the creep strength at normal testing temperatures by extrapolation without serious errors arising.



**The Problem of the Safety of Boiler Tubes with regard to Internal Pressure at High Temperatures.** C. A. Duckwitz and H. Buchholtz. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Nov., pp. 235-242). The authors report the results of internal pressure tests and creep tests in accordance with the German standard creep-testing procedure A117/118 on boiler tubes of unalloyed 0.12% carbon steel, some of which were tempered and others normalised after cold drawing. The time to fracture at temperatures in the 450-600° C. range was determined. The creep strength at 600° C. as determined by this short-time standard method exceeded the stress required to cause rupture within 10,000 hr. by the application of internal pressure. By tempering in the stressed condition at 550° C. a coarser grain size was obtained and the creep strength considerably increased without any increase in the stress at fracture. The recrystallisation temperature is the upper limit of the temperature range in which the strength of the steel increases; above this limit the combined effect of mechanical stress, high temperature and time causes first a coagulation of the cementite and then, as the deformation increases, a coarsening of the grain size; this leads to a reduction in tensile strength but at the same time to an increase in the creep strength. With increasing time under load at above the recrystallisation temperature the material begins to fail at the grain boundaries, numerous intercrystalline discontinuities occur and the cracks spread more and more along the crystal boundaries. A coarse-grained structure evidently has a marked tendency to form intercrystalline cracks at high temperatures.

**Creep-Strength and Internal-Pressure Tests on Welded Tubes of Mild Unalloyed Steel.** C. A. Duckwitz. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Dec., pp. 285-289). The author subjected welded tubes of mild unalloyed steel (St 35.29 with 0.12% of carbon) to tensile tests (between 20° and 600° C.), creep tests (German standard method A117/118, at 400° to 600° C.) and internal-pressure tests. He tested tubes welded with circumferential as well as with longitudinal beads. Both types of joint were oxy-acetylene butt welds. The creep tests confirmed an observation made previously on other qualities of steel, *viz.*, that the creep strength of the welds is, as a rule, superior to that of the unwelded material. The internal pressure tests on tubes with longitudinal welds indicated that the magnitude of the breaking stress for testing periods of 1000 to 10,000 hr. was affected neither by heat treatment nor by machining of the welds, and agreed with the values obtained when testing unwelded tubes and tubes with circumferential beads. These results lead to the conclusion that in the case of soft unalloyed steel the resistance of tubes to static internal pressure at high temperatures is not lowered by welds, and that it does not matter whether these are in the original state or have been heat-treated or machined.



**Brittleness and Damage to Heat-Resisting Steels when Subjected to Creep Stresses.** A. Thum and K. Richard. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, July, pp. 33-42). The authors discuss the cause of the brittle fracture of low-alloy heat-resisting steel bolts under high temperature service conditions.

Experiments with plain and notched bars of various heat-resisting steels under prolonged static loading, mostly at 500° C., show that up to 16,000 hr. no indication of a limiting creep stress is to be found. Chromium-nickel-molybdenum steels showing a tendency to embrittlement have their creep resistance markedly lowered by notches, the effect being considerably greater than would be assumed from short-time creep tests. On the other hand, steels not subject to embrittlement may even have their creep resistance increased by notches. The total deformation at fracture may either increase or decrease with increasing time of loading, according to the embrittling properties of the steel.

Steels which become brittle at 500° C. without load diminish in impact strength more rapidly if kept under load, becoming more brittle the longer the loading period. There is thus a close relation between temper-brittleness and tendency to brittle fracture in creep. Steels not subject to temper-brittleness also show a falling off in impact strength, but only when within the region of brittle fracture. If the damaging stress has not been reached, the impact value can be restored by heat treatment, but not after higher stresses. Specimens which have been broken in creep therefore retain, in their highly stressed parts, their brittle character even after heat treatment, but an intermediate treatment before fracture can restore the property of elongating before rupture.

A determination of temper-brittleness without load is not a sufficient indication of the properties of the steel. It is advisable to carry out annealing under load, provided that this is not too high. As the load increases, the damage line shifts to shorter times. For a low alloy nickel-chromium-molybdenum steel the range within which rupture takes place without deformation is from 360° to 650° C. More highly alloyed steels may be stable at 500° C., but brittle at higher temperatures. Chromium-molybdenum steels without nickel, with or without vanadium or tungsten, may show brittleness. Increase of carbon and silicon influences the creep properties favourably.

**The Embrittlement of High-Chromium Steels in the 300-600° C. Temperature Range.** G. Riedrich and F. Loib. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Oct., pp. 175-182). The authors report on an investigation of the embrittlement of specimens of 48 chromium steels containing from 5% to 29% of chromium after quenching from various temperatures in the 300-600° C. range.

With up to about 15.5% of chromium there was no embrittlement. Steels with 15.5-18% of chromium were fairly brittle and with 19% and more they were very brittle. The quenching temperature range

which caused brittleness was 400–500° C., the greatest brittleness occurring after quenching from 475° C. Increasing the holding time increased the brittleness. The effect of additions of titanium, columbium, manganese, silicon and carbon on the embrittlement tendency was also examined. Both titanium and columbium, when added separately, increased the brittleness. After quenching from 475° C. the amount of chromium necessary to cause brittleness was somewhat higher with 3% of manganese in the steel than when the normal percentage of manganese was present. Up to 2.8% of silicon did not affect the minimum amount of chromium required to produce brittleness, but it shortened the holding time necessary to cause brittleness. Changes in the carbon content in the 0.04–0.28% range had only a very slight effect on the embrittlement tendency. The form of annealing treatment to eliminate the brittleness is discussed.

**Preliminary Test Results for Chromium-Molybdenum-Vanadium Steel "EI-10" for the Connection of Flanges Operating at Temperatures of 450–500° C.** W. Larichev. (Iron and Steel Institute, 1942, Translation Series, No. 86). This is an English translation of a Russian paper which appeared originally in *Sovyetskoye Kotlo-turbo-Stroyeniye*, 1940, No. 3, pp. 107–111.

**The Detrimental Effect on Elongation and Reduction of Area when Steel is Annealed in Hydrogen.** E. Houdremont and H. Schrader. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Aug., pp. 87–94). The authors report on an investigation of the tensile properties of specimens of unalloyed, and of low- and high-alloy steels after annealing at different temperatures and for different periods in atmospheres containing hydrogen. The hydrogen causes embrittlement, even when quite small quantities are present in the furnace atmosphere. Fine internal cracks form in the region of the fracture. The amount of hydrogen necessary to cause the embrittlement is much less than that required to form flakes. Austenitic chromium-nickel steels are not so sensitive, although after long annealing there is some deterioration of the tensile properties. The hydrogen can be expelled from unalloyed and low-alloy steels by heating to 100–200° C., but the temperature must be raised to 500–600° C. in the case of the high-alloy austenitic steels. Tests at down to –80° C. showed that steels which have absorbed a little hydrogen become more brittle as the temperature is reduced; but if a lot of hydrogen has been absorbed the cooling expels some of it, and this causes an improvement in the elongation and necking; on lowering the temperature still further the steel becomes brittle again.

**The Effect of Hydrogen on the Ductility of Steel.** (Metallurgist, 1941, vol. 13, Oct., pp. 36–39). Some recent papers on the effect of hydrogen on the properties of steel are reviewed with particular reference to one by Houdremont and Schrader (*see preceding abstract*).

**Investigation of the Nitrogen Absorption of Pure Molten Iron and of the Alloys Fe–C, Fe–P, Fe–Cr.** T. Kootz. (*Archiv für das Eisen-*

hüttenwesen, 1941, vol. 15, Aug., pp. 77-82). The author describes a fairly simple apparatus with which the amount of nitrogen which can be absorbed by melts of pure iron and some iron alloys was determined. A lime-alumina slag was first prepared and melted in a crucible, and the sample was inserted in the solid state and then melted under the slag. Nitrogen was bubbled through the melt by dipping a fine corundum tube below the slag. At 1600° C. and atmospheric pressure Armco iron absorbed 0.046% of nitrogen, the solubility increasing only very slightly with increasing temperature. The solubility changed with changes in the partial pressure of the nitrogen in accordance with Sieverts' square-root law. The presence of either carbon or phosphorus considerably decreased the amount of nitrogen taken up, whereas increasing the chromium content up to 10% greatly increased the nitrogen solubility; with further chromium additions the solubility decreased.

**Elastic Properties of some Alloy Cast Irons.** A. I. Krynitsky and C. M. Saeger, jun. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Jan., pp. 73-93). The authors report on an investigation of the transverse strength properties of test bars 1.2 in. in dia. and 21 in. in length of three types of alloy cast irons vertically cast, superheated and bottom-poured in green sand moulds at temperatures of 100°, 150°, 200° and 250° C. above the liquidus. The three irons were: a nickel-molybdenum iron (type *L*); a nickel-molybdenum-chromium, low-manganese iron (type *M*); and a nickel-molybdenum-chromium, high-manganese, high-silicon iron (type *N*). The maximum heating temperature had no effect on the transverse strength of irons *L* and *M*, but the moduli of rupture of iron *N* were somewhat higher for the heating temperatures of 1600° and 1700° C. than for 1400° and 1500° C. The highest moduli of elasticity of all the bars tested were obtained with iron *N* which had been heated to 1700° C., but in general no definite relation could be established between the relative moduli of elasticity and the maximum heating temperatures.

**Cast Iron in Relation to Engineering.** E. J. L. Howard. (Journal of the Institution of Production Engineers, 1942, vol. 21, Mar., pp. 103-116). The author discusses how improvements in the strength of cast irons have been brought about in the last ten years. The effects of carbon, silicon, nickel, chromium, molybdenum and copper are dealt with in turn and information is given on the properties of inoculated irons, Meehanite, Ni-tensile iron and Emmel iron. The last-named has a low carbon content and is made with a high proportion of steel scrap; a typical Emmel iron contains total carbon 2.5%, silicon 2.6% and phosphorus below 0.1%, and this would have a tensile strength of 20 tons per sq. in.

**The Influence of Molybdenum and Titanium Additions upon the Properties of a Chrome-Vanadium High-Speed Tool Steel.** D. W. Rudorff. (Stal: Metallurgia, 1942, vol. 25, Mar., pp. 131-133). The author reports the results of an investigation by Shvirev and



Goldvasser at the Leningrad Institute of Metals on the influence of molybdenum and titanium on the cutting properties of 11%-chromium, 2.2%-vanadium high-speed steel. The effects of repeated and prolonged tempering upon the hardness, microstructure and residual austenite content were examined and the results are given in numerous graphs. The cutting properties of the steels after various forms of heat treatment were compared with those of 18/4/1 high-speed steel and the tool life of the steel with 3.8% of molybdenum was practically equal to that of the 18/4/1 steel, whilst that of the steel with 0.3% of titanium was very much shorter.

**The Influence of Tin on Alloy Steels.** G. R. Bolsover and S. Barraclough. (Iron and Steel Institute, 1942, this Journal, Section I.). The authors have investigated the effect of tin, in amounts not exceeding about 0.5%, on the mechanical properties and particularly the notched-bar impact values of seven of the most used alloy steels, with relatively high and low phosphorus contents, a plain carbon steel being included as a basis of comparison; the influence of molybdenum in conjunction with tin was also noted. The steels comprised a 0.35% carbon steel, a manganese-molybdenum steel, a 3½% nickel and a 3% nickel-chromium steel suitable for oil-hardening, two 3% nickel-chromium-molybdenum oil-hardening steels, one with 0.20–0.25% and the other with 0.4–0.5% of molybdenum, a 3% chromium-molybdenum oil-hardening and nitriding steel and a 4¼% nickel-chromium-molybdenum case-hardening steel.

The general effect of tin on the properties of the steels in the hardened and tempered condition and of molybdenum in counteracting that of a high tin content is shown, and further data indicate the influence of tin on the nitriding steel after a blank nitriding operation and on a case-hardening steel in the quenched condition.

**Effect of Phosphorus and of Various Alloying Elements on the Temper Brittleness and Hot-Brittleness of Structural Steel.** E. Maurer, O. H. Wilms and H. Kiessler. (Stahl und Eisen, 1942, vol. 62, Jan. 29, pp. 81–89; Feb. 5, pp. 115–116). The authors report on an investigation of the tendency to temper brittleness and hot-brittleness of 56 different unalloyed and low-alloy steels in which the effect of manganese, nickel, carbon, phosphorus, molybdenum and columbium and the form of heat treatment was studied. Hot-brittleness was induced by long-time annealing at 450° C., and this caused a greater reduction in the notched-bar impact value than did cooling in "Sterchamol" at 2° C. per min. from the tempering temperature. Nickel, manganese, chromium and phosphorus all tend to increase the temper brittleness. Unalloyed steels and steels alloyed with small quantities of these elements have no temper-brittleness tendency if the carbon is very low, as this phenomenon depends on the presence of a certain minimum amount of carbon. Molybdenum decreases the temper brittleness and can even prevent it altogether; there is a critical molybdenum content which produces

the optimum effect. Columbium has almost as favourable an effect as molybdenum. Raising the hardening temperature increases the subsequent temper brittleness. When the ratio of the notched-bar impact strength in the original state to that in the tempered state is plotted against the hardening temperature, there is a temperature range in which the curve rises sharply. Slow cooling from the hardening temperature increases the brittleness of steels having a slight temper-brittleness tendency and has the opposite effect on steels in which this tendency is marked. There is no relationship between the cooling rate and the brittleness of medium sensitive steels. Long-time annealing at a temperature below  $A_1$  but above the critical temperature range referred to previously considerably reduces the subsequent temper-brittleness tendency, which is in agreement with the conclusions of earlier investigators. The results here reported do not confirm statements in the literature that the precipitation of phosphides is the direct cause of temper brittleness. A comparison of a chromium-nickel-phosphorus steel with strong tendency to hot and temper brittleness and a copper-bearing steel having a precipitation-hardness tendency shows that these two phenomena are of different nature.

**True Economy in the Use of Chromium and Nickel.** M. A. Hunter. (Metal Progress, 1942, vol. 41, Jan., pp. 49-51). The author criticises a suggestion by the Metals Priority Division of the Office of Production Management (in the United States) that arbitrary reductions should be made in the amount of nickel used in the production of nickel-steel castings which normally contain 60% and 35% of nickel. He quotes examples where decreasing the nickel content would shorten the life of the part by two-thirds, with the result that the necessary replacements would actually require more nickel for a given service life than if the original nickel content were maintained.

**Possible Alternates for Nickel Chromium Alloy Steels.** (Steel, 1942, vol. 110, Feb. 9, pp. 70, 99, 100). The American Iron and Steel Institute was asked by the War Production Board to undertake a study of possible substitutes for structural steels containing chromium and or nickel. A committee was set up, and its report has been issued as No. 5 in the series entitled Contributions to the Metallurgy of Steel. An abridged version of the report is presented; in it reasons are given for recommending certain maximum amounts of alloying elements to be added to steel.

**Non-Ageing Non-Magnetic Wrapping Wires.** R. Weihrich. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Sept., pp. 153-154). The author reports on his study of the mechanical properties and the corrosion resistance of various non-magnetic steels for making wrapping wire, particularly that for holding armature windings, dealing especially with austenitic manganese-nickel-chromium steels containing 10-17% of chromium, which, on account of their high corrosion resistance, prove particularly satisfactory in practice.



**Government Specifications for Aircraft Steel.** (Iron Age, 1942, vol. 149, Feb. 19, pp. 62-65). Tables of specifications of stainless, carbon and alloy steels for aircraft to the requirements of the United States Army and Navy are presented. The specification number and date, and the composition and important characteristics of each steel are given.

**Structural Steel for the Pressure Parts of Marine Boilers.** (British Standards Institution, 1942, No. 14). This specification constitutes the second revision of the standard first issued in 1904.

## METALLOGRAPHY AND CONSTITUTION

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**Photography of Metals.** H. J. Taffs. (Metallurgia, 1942, vol. 25, Feb., pp. 95-97; Mar., pp. 125-128). The author considers the photography of metals under the three main headings: Straight photography, photomicrography, and low-power photomicrography and macrography. In the first part the apparatus required, preparation of the subject and the taking of the photographs are described and discussed, and the second part is devoted to the illuminating systems and apparatus required for photomicrography and macrography.

**Macrographic Examination of Metals.** N. Metcalfe. (Canadian Metals and Metallurgical Industries, 1942, vol. 5, Jan., pp. 2-5, 9). The author describes macrographic methods of testing steel and gives illustrated examples of results obtained and their interpretation. These examples include determining and specifying the case depth of a hardened part, detecting cracks and making sulphur prints.

**Microscopic Determination of the Ore Minerals.** M. N. Short. (United States Geological Survey, 1940, Bulletin 914). The author describes improvements in the methods of identifying ore minerals which have been developed since his first report on this subject in United States Geological Survey Bulletin 825 (*see* Journ. I. and S.I., 1931, No. II., p. 494). The present report is in four parts dealing with: (1) Microscope technique; (2) physical properties and measurements; (3) etch reactions and determinative tables; and (4) microchemical methods. In the fourth part the procedures for testing for a large number of elements are given.

**The Electrolytic Polishing of Metals.** P. Schafmeister and K. E. Volk. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Nov., pp. 243-246). The authors review the literature on the electrolytic polishing of metals and compare results obtained by mechanical and electrolytic methods. An advantage of the latter process is that no mechanical deformation of the surface can take place, whilst a disadvantage is that heterogeneous surfaces are unsuitable for electrolytic polishing when the different phases have

different electro-chemical properties, for the less noble phases will dissolve more quickly leaving pits.

**The Difference between Elastic Constants Determined Mechanically and by X-Rays.** F. Bollenrath, E. Osswald, H. Möller and H. Neerfeld. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Oct., pp. 183-194). It had been noted that when determining elastic constants of polycrystalline iron at the Kaiser-Wilhelm-Institut für Eisenforschung, there was always a difference between the results obtained by mechanical means and X-rays, whereas the results obtained by the two methods at the Deutsche Versuchsanstalt für Luftfahrt were in close agreement. Experiments were therefore made at the two Institutes on the same bars, with the same load and by the same experimental method in order to ascertain the reason for these differences. Apart from small residual differences, which did not affect the elastic constants, the results were in good agreement. It is concluded that differences between the mechanical and X-ray values are always present, and that occasional agreement is only accidental. The differences are attributed to the elastic anisotropy of crystals in an aggregate. An attempt has been made to calculate the X-ray values on the basis of a physically acceptable hypothesis as to the behaviour of aggregates. Experiments are in hand to take into account the crystallographic orientation of the reflecting crystals in the measurement of stress. The cause of the original differences between the two Institutes has not been fully determined, but it is established that no fundamental difference exists.

**A New Electrolytic Isolation Method for the Determination of Iron Carbide.** E. Houdremont, P. Klinger and G. Blaschczyk. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, Dec., pp. 257-270). After an extensive review of the literature on the isolation of carbide from cast iron and steel, the authors describe at some length their new electrolytic method, the advantage of which is that, owing to the use of a neutral electrolyte and the suppression of oxygen at the anode, the carbide is not decomposed by secondary reactions. With the aid of this method they were able to prove that  $\text{Fe}_3\text{C}$  is the only iron carbide ever occurring in steel, independent of the heat treatment to which the steel has been subjected and of whether it is hypo- or hyper-eutectoid. All the other iron carbides mentioned in the literature are formed during the isolation only, *i.e.* by decomposition of  $\text{Fe}_3\text{C}$ . The investigation showed further that no chromium carbide is present in low-chromium alloy steels.

**Woody Fractures.** R. K. Kulp. (Iron and Steel Engineer, 1942, vol. 19, Feb., pp. 39-59). After reviewing the literature on fractures in steel which have a woody or fibrous appearance, the author describes the numerous tests made at an American steelworks in order to trace the cause of this type of fracture appearing in nick-break tests. The appearance of the fracture improved with increasing rate of fracture. The frequency with which woody fractures

occurred increased with decreasing thickness of the plate down to  $\frac{1}{4}$  in., at which thickness most of them were quite woody in appearance. The method of making the notch did not affect the fracture obtained. Vacuum-fusion analyses for gases indicated that woody fracture samples contained about twice as much hydrogen and nitrogen as those with a crystalline fracture.

**The Capillarity in the Grain Boundaries of Metals. Its Effect on the Grain Growth and Its Importance in Steel.** C. Benedicks. (*Kolloidzeitschrift*, 1940, vol. 91, No. 3, pp. 217–232). The author points out that there are two fundamentally different types of grains in metals, *viz.*, “accidental” and “capillary” grains. Accidental grains are formed primarily, *e.g.*, on solidification of metals. Their surface area is large, and owing to the effect of capillary surface tension they are liable to be transformed into grains with a minimum surface area, *i.e.*, the so-called capillary grains. The author deals at some length with the theory of the surface tension as effective in the grain boundaries of metals. He suggests that, as in liquid systems, it will be affected by foreign substances, and that there are two types of foreign substances, *viz.*, “horophilic” and “horophobic” ones. The latter, which are of minor practical importance, slightly increase the surface tension and will therefore migrate away from the grain boundary. The former greatly decrease the surface tension, so that they accumulate in the grain boundary and counteract grain growth. In this way the stability of the grain structure is increased. At the same time, however, the cohesion between neighbouring grains will become smaller, so that the strength of the material is lowered. This leads to the conclusion that grain-stabilising elements should be present in minute concentrations only. He points out that the accumulation of foreign substances in the grain boundary is particularly important if they cause increased hardness there. He refers in this connection to some elements which, owing to the formation of very hard nitrides, are particularly effective in stabilising the grain boundaries, and briefly summarises the results obtained by Ljunggren when studying this phenomenon with the aid of the sclero-grating method (*see Journ. I. and S.I.*, 1940, No. I., p. 341 p). Finally the author points out that the sensitivity to overheating is lowered by stabilisation of the grain boundaries, which has a favourable effect on the “body” of the steel.

**The Iron/Iron-Sulphide/Calcium-Sulphide System.** R. Vogel and T. Heumann. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Oct., pp. 195–199). To obtain information on the effect of a third element on molten iron high in sulphur, the authors investigated the iron/iron-sulphide/calcium-sulphide system. The boundary areas of the iron-sulphide/calcium-sulphide and the iron/calcium-sulphide systems were first studied. Iron sulphide and calcium sulphide form a simple system with a eutectic, and the possibility of the solid-solubility of iron sulphide in calcium sulphide remains open. An upper limit

to the melting point of calcium sulphide was determined from the course of the liquidus curve; this limit was at  $2450^{\circ}\text{C}$ . Liquid calcium sulphide and iron are practically immiscible. The equilibrium conditions for the ternary system were determined. The ternary diagram is characterised by a miscibility gap for the liquid state which extends from the 100% miscibility gap between iron and calcium sulphide to a lower critical point at about  $1800^{\circ}\text{C}$ ., as well as by a ternary eutectic point the temperature of which is practically the same as that of the iron/iron-sulphide eutectic. The experiments with the calcium sulphide used pointed to equilibria between calcium sulphide, calcium sulphate, calcium oxide and sulphur. The effect of calcium on high-sulphur iron is discussed on the basis of the experimental results.

## CORROSION OF IRON AND STEEL

**The Transcrystalline Stressed Crack Corrosion of Steel.** H. Buchholtz and R. Pusch. (Stahl und Eisen, 1942, vol. 62, Jan. 8, pp. 21–28). The authors report on an investigation of the nature and causes of cracks in the steel cylinders and pressure vessels used for storing town gas and long-distance gas under high pressure. These cracks run parallel to the longitudinal axis of the cylinder and are characterised by their transcrystalline path without the formation of slip planes. The cracks were found to be due primarily to the action of hydrocyanic acid in the condensate formed by the impurities and the moisture in the gas on the stressed steel. The degree of attack increased with the concentration of the acid, the time of contact and the elastic stress applied to the steel. The crack depth increased more rapidly with low-alloy and heat-treated steels than with mild steels. With actual gas cylinders the incidence of cracks in low-alloy and heat-treated steels is all the greater because they are subjected to higher stresses. The initiation of the first cracks is not fully explained by theories of corrosion-chemistry, but the mechanical stresses, the stress concentration at the bottom of the crack and the crack-sensitivity of the steel are important factors in the spreading of cracks. To prevent their formation, drying the gas and the removal of cyanides are recommended. When this cannot be done, zinc or aluminium coatings give satisfactory protection to the steel.

**Resistance to Cavitation Erosion.** R. Beeching. (Institution of Engineers and Shipbuilders in Scotland: Engineering, 1942, vol. 153, Mar. 20, pp. 238–240; Apr. 3, pp. 278–280; Metallurgia, 1942, vol. 25, Feb., pp. 109–112). The information on the causes of cavitation erosion in ships' propellers and pump impellers is reviewed and the following conclusions are arrived at with regard to the mechanism of the attack: (1) Cavitation erosion results primarily



from the repeated deformation of the surface layers of a metal exposed to the attack, as a result of the high shear stresses produced in the metal by the pressure impacts caused by the collapse of cavities in the fluid; in severe cases the stresses arising will exceed the fatigue limits of the most resistant materials. (2) As a result of the repeated application of stresses exceeding the "pitting limit" of McAdam, the corrosion of the surface may be accelerated; in turn, this corrosion will accelerate the mechanical disruption of the surface. (3) For an alloy to have a high resistance to this form of attack, it should have a high resistance to repeated stressing above the fatigue limit as well as a high resistance to corrosion even when repeatedly stressed. A vibratory method of making laboratory tests of the resistance to cavitation erosion is described and some results with non-ferrous alloys and cast irons are presented and discussed.

**Observations on Corrosion Damage.** F. Borsig. (Stahl und Eisen, 1942, vol. 62, Feb. 26, pp. 174-179). The author describes some examples of damage to machinery, particularly turbines, caused by corrosion. The examples include corrosion by wet steam and corrosion damage to the blades of idle turbines due to percolating vapours. The results are presented of some tests in which turbine blades of a 5%-nickel steel were suspended in a small tower in which a mixture of water vapour and air was passed over them; the protective effect of coating the blades with different kinds of oil was studied by these tests and it was found that emulsifiable oils gave much better protection than engine oil and paraffin.

**The Reversal of Polarity of an Iron-Zinc Couple in Aqueous Solutions due to the Formation of a Protective Film.** H. Roters and F. Eisenstecken. (Archiv für das Eisenhüttenwesen, 1941, vol. 15, July, pp. 59-62). The authors report on some experiments in which the changes of potential of iron-zinc couples in a 1% solution of common salt and in distilled water were measured. The couples consisted of specimens of steel and galvanised steel, and of pure zinc and zinc-iron alloys. In course of time the zinc (or galvanised) element became the positive pole. The absolute negative value of the zinc potential was not so high as that of the iron, which remained constant at about -440 mV. The current strength after the reversal of polarity was always very small. The quantity of iron dissolved by the galvanic action was very small in comparison with the loss of weight of steel specimens not connected to zinc, which rusted. This reversal of polarity which can take place after a certain time interval with zinc-iron couples is interesting from the electro-chemical aspect, but has no practical significance with regard to galvanising as a means of protecting the surface of steel water-pipes against corrosion.

**Soil-Corrosion Studies, 1939. Coatings for the Protection of Metals Underground.** K. H. Logan. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Jan., pp. 57-71). The author reports the results of soil-corrosion tests on iron and steel



sheets and pipes which have been conducted by the National Bureau of Standards for periods of two to sixteen years in order to test the relative merits of different protective coatings. An earlier conclusion that lead coatings are inadequate for protecting iron and steel underground was confirmed. After exposure to soils for fifteen years, two hot-dipped asphalt and coal-tar coatings were found to have failed. Of a group of experimental coatings tested for seven years, a vitreous enamel coating and two hard rubber coatings afforded complete protection. Of a group of coatings tested for two years, a bakelite coating consisting of several coats of bakelite varnish, each coat baked on, afforded the most satisfactory protection; air-dried bakelite coatings blistered somewhat and permitted some rusting.

**An Accelerated Atmospheric Corrosion Test.** H. Pray and J. L. Gregg. (Proceedings of the American Society for Testing Materials, 1941, vol. 41, pp. 758-765). The authors describe a procedure for corrosion testing which comprises four weeks' exposure in the atmosphere to produce an initial rust film, followed by two weeks' exposure in an apparatus which is described in detail. It was found that no combination of conditions in the apparatus would duplicate the results obtained by initial exposure to the atmosphere so that a preliminary four weeks' exposure was necessary; the results obtained after the combined test of six weeks were, however, equivalent to the effects of several years' exposure. The apparatus in question consists of a revolving rack capable of carrying 96 suspended specimens each 12 in.  $\times$   $\frac{3}{4}$  in. so mounted that they travel through three compartments. The largest compartment is one of high humidity; a small glass-walled compartment is used for drying, and the third is a refrigeration compartment. The most satisfactory testing conditions were obtained by revolving the carrier at three revolutions per hr. In one revolution each specimen is wetted for 15 min., dried for 2.5 min. and cooled for 2.5 min.

## BOOK NOTICE

MEYENBERG, F. L. *Economic Control of Iron and Steel Works.* With a Foreword by Sir William Larke, K.B.E. 8vo. pp. xx + 332. London, 1942: Chapman & Hall, Ltd. (Price 25s.)

Sir William Larke, who has written a foreword, concludes with the following words:

"Universities and technical schools and colleges might include in their curricula, with great advantage, a course of lectures on the subject matter of this book, for degrees in metallurgy and engineering."

This sums up excellently the views of the present writer after studying Mr. Meyenberg's work. It seems equally desirable that the office

men, the accountants responsible for the works and financial accounts, &c., should have some actual first-hand experience in works production problems as part and parcel of their training.

Unfortunately, the office man and the works man generally travel a different road; they glimpse each other from a distance, and occasionally one or the other crosses the barrier for a brief conference as to where they are going. \*

Meyenberg has set himself the task of removing the barrier that separates the pilgrims. As he says in his preface :

“The second purpose of the book is to contribute to a better understanding between the various groups of industrial employees engaged in the same works, but trained in different professions and working frequently not in the spirit of co-operation needed at present more urgently than at any time since the beginning of industrial activity. It is the conviction of the author that this co-operation cannot be brought about for long by compulsion, but can only be created and maintained if based on the mutual understanding of the various parties so essential to the success of their work.”

The author divides his work into five parts. The first three parts are devoted to the problem of accounts, and he attacks with great enthusiasm the difficult task of really interesting the technical man in the intricacies of cost-accounting, the connection between works, financial and job accounts. Part 4 is devoted to the problem of standard costs and will no doubt make a more direct appeal to the works man than the earlier chapters. The last part of the book, “The Organisation of Economic Control,” is the shortest, but is probably the most important; here the author sums up the lessons learned in the previous four parts, brings all the strings together, and finally, in Chapter XXI., propounds his solution of the problem.

This is certainly a book which every departmental manager should have in his library, and my advice to him, if I were asked, would be : Read Part 5 first and you will be all the more eager to read and master the detailed exposition given in the earlier parts of the book.

N. H. BACON.

## ORES—MINING AND TREATMENT

(Continued from p. 2 A)

**Concentration of Manganese Ores from the Drum Mountain District, Utah.** S. R. Zimmerley, J. D. Vincent and C. H. Schack. (United States Bureau of Mines, Manganese Investigations No. 1, 1942, Jan., Report of Investigations No. 3606). The authors give an account of their investigations of suitable methods of concentrating high-, medium-, and low-grade manganese carbonate ores from the Drum Mountain district of Utah. The high-grade selectively mined ore was found readily amenable to concentration; 96.6% of the manganese in the ore was recovered as a sand product, which, when sintered, met the chemical specifications for ferro-manganese for steelworks. A medium-grade ore (manganese 22.9%), made by recombining samples of selected ore and rejects, was concentrated to a suitable grade, approximately 80% of the manganese being recovered. The low-grade ore (manganese 14.9%) was also concentrated; much clay and fine sand were rejected before milling, and 89.4% of the manganese actually milled was recovered as a final ferro-manganese sinter; calculations based upon the ore and clay actually mined showed a recovery of about 70% of the total manganese.

**Recovery of Manganese from Chamberlain Nodules by the Reyerson Modification of the Sulfur Dioxide Leaching Process.** C. E. Wood, C. L. Wallfred, E. P. Barrett, L. J. Reader, S. I. Ginsberg, W. F. Wyman and R. L. Evans. (United States Bureau of Mines, Manganese Investigations No. 2, 1942, Jan., Report of Investigations No. 3609). The authors report on their tests of the application of a modification of the sulphur-dioxide leaching process for the leaching of manganese-carbonate ores which occur at Chamberlain, South Dakota. These ores are known as Chamberlain nodules. In the Reyerson modification of the sulphur-dioxide process, manganous sulphate in dilute solution is used as a catalyst for the production of sulphuric acid from mixtures of sulphur dioxide and air. Three types of equipment were tested on a laboratory scale. The highest manganese recovery was obtained with a spray leacher in which a slurry of nodules was treated in batches with sulphurous gases. The tests indicated that an 85% recovery of manganese could be obtained in an extraction period of 2-3 hr. if a 10-15% solution of manganous sulphate was produced.

**Our Metallurgical Chrome Ore Requirements.** J. Strauss. (Bulletin of the Mining and Metallurgical Society of America, 1942, vol. 35, Jan., No. 264, pp. 3-8). The author refers to the difficulty of continuing the large-scale production in the United States of ferro-chromium alloys with a chromium/iron ratio of at

least 3 to 1. He discusses the influence of ore size on the preparation of high-carbon and low-carbon ferro-chromium, and suggests that chemical extraction methods be adopted to remove some of the iron and gangue from the ore in order to prepare a high-chromium concentrate.

## REFRACTORY MATERIALS

(Continued from p. 3 A)

**Our Refractory Chrome-Ore Requirements of the Refractory Manufacturers and the Steel Industry.** G. E. Seil. (Bulletin of the Mining and Metallurgical Society of America, 1942, vol. 35, Jan., No. 264, pp. 8-11). The author discusses the different characteristics of chrome ores for metallurgical and for refractory purposes, and the methods of converting magnesium metasilicate to the orthosilicate, the latter having much better refractory properties.

**Basic Refractory Practice at Algoma Steel Corporation, Ltd.** J. W. Craig. (Blast Furnace and Steel Plant, 1942, vol. 30, Feb., pp. 241-245). The author describes some of the experience gained in the lining of basic open-hearth furnaces at the works of Algoma Steel Corporation, Ltd., Sault Ste. Marie, Ontario. Excellent results were obtained with a chemically bonded proprietary ramming material with a magnesia base on the furnace bottom, as well as with a graded, chemically bonded plastic of non-slaking magnesite and chrome ore for the tapholes. Magnesite-chrome bricks with an abnormally high spalling resistance are used for the front walls and for the mixer lining. The back walls are made of magnesite bricks, with a facing of large lumps of a hard South African chrome ore.

**Electric Steel-Plant Refractories.** J. H. Chesters. (Iron Age, 1942, vol. 149, Mar. 12, pp. 53-59). The author describes the construction of linings for 10-ton basic electric arc furnaces. Most arc-furnace roofs are made with silica brick, but the marked maturing observed with open-hearth furnace roofs does not seem to take place in the arc furnace, possibly because the surface layers melt away before they have time to mature, or perhaps because of the strongly reducing atmosphere. The spalling of the roofs can be largely eliminated by careful handling of the furnace; the melting programme should, if possible, be arranged so that frequent heating and cooling below red heat do not occur. The charging arch is usually built of silica brick, and the tapping arch of magnesite brick. The general technique of installing a rammed or monolithic hearth in an arc furnace is similar to that employed with the open-hearth furnace, but there has been a tendency to use a more finely ground material. In Great Britain the hearth usually consists of



tarred "basic" (dolomite calcined at high temperature), rammed in successive layers and burnt in position by placing coke and old electrodes on the fully rammed hearth and turning on the power for a burning-in period of about 36 hr. With a dry rammed dolomite hearth the metal charged can be relied on to produce adequate sintering of the material.

**Arc Furnace Refractories.** N. F. Dufty. (Iron and Steel, 1942, vol. 15, Apr., pp. 224-228). The author discusses the advantages and disadvantages of different refractory materials for lining electric-arc furnaces. Silica brick is the generally accepted material for the furnace roof, owing to its high refractoriness under load; excessive spalling of these bricks does not occur with removable roofs, because the thickness of brick which is cooled below the critical temperatures during the short time the roof is exposed for charging the furnace is very small. Metal-cased magnesite bricks have shown better results in modern high-voltage arc furnaces than any other material; a side-wall life of 375 heats has been reported for metal-cased magnesite. Chrome-magnesite bricks are not so prone to bursting in arc furnaces as in open-hearth furnaces, because the atmosphere in the former is never strongly oxidising. Below the slag-line stabilised dolomite bricks are the best proposition. The method of ramming in graded dolomite and burning it in to form a hearth is explained. The maintenance of hearths is discussed under the headings: (1) Wear of the furnace bottom; (2) small deep holes in the bottom; (3) erosion of the banks; and (4) building up of the banks or bottom.

**Rammed Linings for Small Electric Furnaces.** H. C. Fisher. (Metal Progress, 1942, vol. 41, Feb., pp. 187-191). The author describes how to prepare and ram linings for a small rotating arc furnace for melting nickel and for a small high-frequency induction metallurgical furnace.

## FUEL

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(Continued from pp. 3 A-6 A)

**Standard Fuel Costs for Reheating Furnaces.** F. Ryder. (Blast Furnace and Steel Plant, 1942, vol. 30, Feb., pp. 238-240). The author explains the object of setting up fuel cost standards for soaking pits and rolling-mill reheating furnaces, and makes several references to the literature on the methods of establishing such standards.

**Metallurgical Furnaces and the Mechanical Stoker.** G. Powis. (Metallurgia, 1942, vol. 25, Apr., pp. 187-188). The author discusses the possibilities of using mechanical stokers in metallurgical practice, and reviews the types of furnace which can advantageously be fitted with them. He makes some suggestions regarding the construction and material of the stokers.



**Selection of Coals for Coke-Making.** J. D. Davis. (United States Bureau of Mines, 1942, Jan., Report of Investigations No. 3601). After discussing the desirable chemical and physical properties of blast-furnace coke, foundry coke, domestic coke and coke for making water-gas, the author describes in detail small-, medium- and full-scale methods of testing coking coals, particularly the Agde-Damm, Davis and Gieseler plasticity tests. Plastic-range tests are of value in studying effects of blending, weathering and petrographic composition on coking properties, but in the present stage of their development they are not adequate for showing precisely the quality of the coke which would be produced from the coal in an industrial plant.

**By-Product Oven Operation under Present-Day Conditions.** W. T. Brown. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 67-71; Feb., pp. 219-223, 226). The author gives a short account of the relation between the geology of some American coking coals and their coking properties, and discusses means of increasing the output of coke-ovens. Control of the amount of volatile matter in the coke is one of the best methods of improving the quality of blast-furnace coke, particularly with fast coking times. Blending some low-volatile coal in the charge, pushing the coke before all the volatile matter is driven out of it, *i.e.*, with 1.0-1.5% of volatile matter, and treating the charge with oil to increase the bulk density are three suggested methods for improving coke-oven output. The addition of low-volatile coal to the charge will slow up the rate of gas evolution, and the gases will be in contact with the oven walls for a longer period, which will facilitate cracking the paraffines. Crushing the coal to a finer particle size will also slow up the flow of gases, with the same result. Improved distillation equipment will improve the quality of the nitration toluene by permitting closer fractionation.

**The Properties of Blast-Furnace Coke.** (Coke and Smokeless-Fuel Age, 1942, vol. 4, Mar., pp. 56-57, 66; Apr., pp. 78-80). There has been for many years a controversy on the desirability or otherwise of using coke of high combustibility in the blast-furnace. Koppers has expressed the opinion that high combustibility is desirable, whereas according to Wüst it is preferable not to have such strong combustion in front of the tuyères, for, if there is less reoxidation of reduced iron in this zone, there would be no additional fuel required for re-reduction. Wüst's arguments in support of this theory are quoted from one of his papers published in 1926. The effect of changes in the coke size and of the relation of coke size to ore size are discussed, with special reference to Mayer's views on the coke size necessary for it to form an open supporting structure in which the ore and limestone can lie exposed to the action of gases.

## PRODUCTION OF IRON

(Continued from pp. 7 A-8 A)

**Blowing-Out of the No. 3 Blast-Furnace at the Magnitogorsk Stalin Metallurgical Works.** G. Pitrovskiy, M. Vdovenkov and A. Dryupin. (Stal, 1940, No. 10, pp. 13-15). (In Russian). A time-table is given of the blowing-out process which was carried out without the addition of any material to fill the empty space in the furnace as the burden was consumed. For blowing out, the furnace was disconnected from the gas main, the furnace gas being allowed to escape to atmosphere. Water was supplied through water-pipes welded into the gas outlet pipes to cool the throat. Additional steam was supplied to the dust-catchers. The essential feature of the blowing-out operation by this method is the control of the throat temperature, which should not exceed about 550° C., for fear of gas explosions. Throat temperature is controlled by controlling the rate of supply of the cooling water and the blast. The latter should be reduced to one half of the original supply towards the end of the operation. The stock level should fall to 1.5-2 m. above tuyère level. The blowing-out operation described took 14 hr. 5 min.

**An Audit of the Carbon, Oxygen and Hydrogen in an Iron Blast Furnace.** J. S. Fulton. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 83-88; Feb., pp. 233-237; Mar., pp. 339-344). The author discusses formulæ for calculating the amounts of carbon monoxide, carbon dioxide and hydrogen in blast-furnace gas from the weight of coke required to produce a ton of pig iron using "standard" air. He stresses that more study should be given to the CO/CO<sub>2</sub> ratio, and that the oxygen in the blast should be considered on a weight basis.

**The "Bottom Reaction" Process for the Production of Vanadium Slag.** G. Naeser and E. Ritter. (Stahl und Eisen, 1942, vol. 62, Mar. 12, pp. 217-222; Mar. 19, pp. 241-245). Many attempts have been made in Germany to develop a process for recovering a substantial proportion of the vanadium which is lost in the converter slag, but no great measure of success has been achieved. In this paper the authors describe the "bottom reaction process," the object of which is to produce a special blast-furnace slag high in vanadium from which the vanadium can be recovered by known methods, and thus substantially to reduce the vanadium content of the metal which is put in the converter. The process was developed from experiments in which a mixture of mill-scale and powdered waterglass was burnt in on the bottom of a ladle; when the basic iron was poured in, a thin slag layer formed on this oxidising agent; this slag floated up in drops to the surface, and reacted with the metal as it passed through it, and took up

vanadium from the iron. For full-scale blast-furnace practice the launder from the taphole was lined with a mixture of mill-scale, phosphoric ore with some sand and soda; the launder widened out into a fore-hearth constructed so that the iron and slag poured over a dam about 20 in. high; this made the slag more fluid and enabled it to be skimmed off. The slag thus obtained had a vanadium content of 1.5–2.5%, equivalent to a recovery of 40–50%.

**The Applicability of Blast-Furnace Slag in the Cement Industry.** R. Grün. (Stahl und Eisen, 1942, vol. 62, Apr. 9, pp. 301–307). In the introduction to his paper the author discusses the economic advantages of the use of blast-furnace slag in the cement industry. He then deals with the four factors which decide the suitability of slag as a component of cement, *viz.*: (1) The chemical composition, especially the proportions of silica, alumina, lime, magnesia, manganese and sulphide; (2) the physical state of the slag, glassy slags set, as a rule, more easily; (3) the granulation and the structure; and (4) the type of the activator developing the hydraulic properties. These activators include (a) alkalis in the form of hydroxides, carbonates, sulphates and silicates; (b) calcium as oxide or hydroxide; (c) various forms of gypsum; (d) lump slag, which may or may not be treated with acid; and (e) Portland cement clinkers derived from natural raw materials or blast-furnace slag, sometimes treated with acid.

**Recent Developments in the Production of Sintered Magnets of Iron-Nickel-Aluminium Alloys.** W. Hotop. (Iron and Steel Institute, 1942, Translation Series, No. 88). This is an English translation of a paper which appeared in Stahl und Eisen, 1941, vol. 61, Dec. 4, pp. 1105–1109. See Journ. I. and S.I., 1942, No. I., p. 219 A.

**Substitutes Iron Powder for Bronze.** A. F. Macconochie. (Steel, 1942, vol. 110, Mar. 16, pp. 98–100, 117). The author briefly describes the powder-metallurgy process of making small bushes and gears from iron powder instead of bronze. The iron powder contains about 1% of combined carbon, and about 2% of graphite is mixed with it before putting it in the die, where it is subjected to a pressure of up to 30 tons per sq. in. After pressing, the parts are sintered at 2000° F.

**Powder Metallurgy.** F. C. Kelley. (Canadian Metals and Metallurgical Industries, 1941, vol. 4, Dec., pp. 322–327). The author reviews recent developments in powder metallurgy, points out the advantages and limitations of the process and discusses the effects of time, temperature and pressure on the density of sintered iron, cobalt and nickel.

**Japanese Iron Economy in the Area of Greater East Asia.** J. W. Reichert. (Stahl und Eisen, 1942, vol. 62, Mar. 26, pp. 265–268). An account is given of the political and economic position of Japan's industries, particularly the iron industry, as well as of the measures now being taken to increase production for war purposes.

**Costs and Prices in the Iron-Producing Industry.** H. Dichgans. (Stahl und Eisen, 1942, vol. 62, Mar. 19, pp. 237-241).

## FOUNDRY PRACTICE

(Continued from pp. 8 A-10 A)

**A Technical Department for the Small and Medium Castings Foundry.** H. Hayden. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Apr. 23, pp. 9-10). The author suggests that it would be advantageous to organise a planning and technical department for foundries by which a greater degree of co-operation would be achieved between the designer, pattern-maker, moulder and pourer than exists at present. Such a department would be particularly useful to foundries now going in for quantity production.

**Improving Cupola Performance.** D. J. Reese. (Foundry, 1942, vol. 70, Feb., pp. 68-69, 140-144). In discussing measures for improving cupola performance under war-time conditions, the author advocates extending the use of compressed-steel turnings, more accurate knowledge and control of the quantity, pressure and velocity of the blast, the use of mechanical charging where the production justifies it, and more accurate control of the amount of metal poured into the ladle.

**Practical Hints on Charge Composition and on Cupola Practice.** E. Diepschlag and C. Stieler. (Giesserei, 1942, vol. 29, Jan. 9, pp. 2-7). The authors make the following recommendations with regard to cupola practice: (1) Different qualities of pig-iron and scrap should be stocked in well-separated heaps, each plainly labelled. (2) In making up charges from different heaps, if possible the amount from any one heap should not exceed 20% of the metal to be charged, as this lessens the risk of trouble due to irregularities in analysis. (3) When different pig irons are mixed in a charge, their melting points should be in as small a range as possible; this is important in foundries using small ladles, because the iron with the lowest melting point will collect at the taphole first, and the first ladle of iron run off will not be representative of the mixture. Some tables of quantities and analyses of correctly and incorrectly made-up charges are presented, and simple calculations are made which show the detrimental effect of the latter on the composition of the iron tapped.

**An Improved Method for Drying and Preheating Ladles.** (Iron and Steel, 1942, vol. 15, May, pp. 272-273). The inefficiency of the usual methods of drying and preheating foundry ladles is pointed out, and a description and drawing are given of an improved burner equipment for this purpose. This equipment consists of a close-fitting lid lined on the under side with refractory material held in



place by expanded metal tack-welded to the lid. Two chimneys symmetrically placed in the lid permit the products of combustion to escape. The burner passes vertically through a collar in the centre of the lid. The burner consists of three concentric tubes. Primary air is fed to the centre tube, the fuel gas to the inner annular space and secondary air to the outer annular space. A loose sleeve may be placed over the burner tip; this ensures that the flame gets well down towards the bottom of the ladle; it also protects the burner head, and is quite easily replaced when necessary.

**Foundry Production Problems with Special Reference to High-Duty Alloy Cast Iron.** A. E. McRae Smith. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 66, Apr. 9, pp. 225-228; Apr. 16, pp. 241-244). The author first reviews the methods of producing high-duty cast irons to comply with the requirements of British Standard 786, Grade 3 (18-22 tons per sq. in. tensile strength) and Grade 4 (min. 25 tons per sq. in.). Reference is made to the structure of alloy cast irons containing molybdenum 0.5-1.5% and nickel 1-5%, the nickel being adjusted to the cooling rate; the acicular structure observed in this iron consists of a series of austenitic decomposition products which form below the pearlitic temperature range by the precipitation of free ferrite and diffusion of carbon into the surrounding austenite. Provided the composition is suitable, a subsequent low-temperature annealing treatment, usually in the neighbourhood of 320° C., will completely change the residual austenite into a wholly acicular structure. In these acicular nickel-molybdenum cast irons maximum toughness is obtained in the as-cast condition if a proportion of the free austenite remains, whereas maximum tensile strength with only a moderate reduction in toughness is obtained after low-temperature heat treatment. Methods of preventing porosity in the casting of cylinder liners, dies for hot-heading, lathe headstock spindles, chucks and gland-rings are described, with particular reference to the feeding arrangements.

**Recent Developments in Sand-Testing.** W. Y. Buchanan. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Apr. 30, pp. 31-34; May 7, pp. 51-54). The author makes a comparative survey of British and American methods of testing moulding sand. He first analyses the present position of sand-testing in the two countries and then discusses the controversy on methods of preparing test specimens and the present organisation of research on moulding sand in Britain.

**Running and Feeding Malleable Iron.** E. Holland. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Apr. 23, pp. 13-14). The author discusses the liquid shrinkage and solid contraction of malleable cast iron, and makes recommendations on the use of denseners and the position of feeders for malleable iron castings.



**Control in the Repetition Foundry.** A. B. Bill. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Apr. 30, pp. 25-29; May 7, pp. 45-49). The author describes foundry practice and methods of dealing with difficulties in the production of large numbers of small malleable iron castings. It is recommended that denseners, feeders and ties should become an integral part of pattern equipment and not be left to the discretion of the moulder. Ramming should be controlled, for improper ramming is the cause of as many rejects as any other single factor. Other points dealt with are jigs for positioning cores, rapid notification of faults to prevent additional wasters being cast and the inspection of patterns and castings.

**Some Critical Notes on Moulding and Casting Technique.** F. Surau. (Giesserei, 1942, vol. 29, Feb. 6, pp. 46-47). The author criticises some of Lehmann's proposals for German standards relative to gating practice (*see* Journ. I. and S.I., 1942, No. I., p. 88 A).

**Treatment of Porosity in Hydraulic Castings.** R. C. Dyer. (Foundry Trade Journal, 1942, vol. 67, May 7, p. 58). The author briefly describes a method of dealing with slight porosity in castings which have to stand a hydraulic pressure test. On locating the porosity, the area was drilled to half the thickness with a small bit, a nipple was screwed in, a liquid synthetic resin was injected under pressure and the hole was then plugged. The casting was baked at about 200° F. in a core-oven overnight. Castings which had at first leaked under test at 50 lb. per sq. in. safely withstood a pressure of 300 lb. after this treatment. These castings have given satisfactory service.

**The Foundry Industry and Air Warfare. Parts I. and II.** (Foundry Trade Journal, 1942, vol. 67, Apr. 9, p. 229: Apr. 16, pp. 247-248). In Part I. some general information on the rôle of castings in aircraft and their accessories is given, and the policy of quality first is stressed. In Part II. a description is given of the pattern, core-making and moulding for casting steel shells for 500-lb. bombs.

**Bed-Plate Casting.** L. Clarke. (Canadian Metals and Metallurgical Industries, 1941, vol. 4, Dec., pp. 332-333). The author describes the preparation of a mould for casting a marine-engine bed-plate 20 ft. long  $\times$  13 ft. wide with the main members  $1\frac{1}{4}$  in. thick.

**Casting Guns Centrifugally at Watertown.** R. W. Case. (Foundry, 1942, vol. 70, Feb., pp. 62-63, 154-156). The author describes developments in gun-making processes at Watertown Arsenal, with special reference to centrifugal casting. This process is now applied in making barrels up to 4.5 in. in internal dia. The moulds consist of long, horizontal tubes up to 10 tons in weight, rotated by a motor. The steel is melted in coreless-induction furnaces, and the whole furnace is transported to the mould for

pouring. The barrels are normalised, tempered, machined and cold-worked; descriptions of these processes are given in general terms.

**Mechanisation of Foundries.** A. S. Beech. (Proceedings of the Institution of Mechanical Engineers, 1942, vol. 147, pp. 53–60). The principal operations in mechanical moulding plants and various types of machines for different classes of work are described. These machines are used for the preparation, reconditioning and transport of sand; mould conveying, pouring and knocking-out; and transport of the empty boxes back to the moulding machines. The respective merits of various classes of moulding machines are discussed; the jolting type is compared with ordinary "straight pressure moulding". Reference is made to the improvements in working conditions which can be effected by mechanisation and by proper ventilation at the knocking-out station. Finally, some examples of fully and semi-mechanised foundries are described, and it is shown how mechanisation can be applied to quite small plants.

## PRODUCTION OF STEEL

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(Continued from pp. 11 A–12 A)

**Determination of the Pin Distribution for Converter Bottoms.** H. Schwiedessen. (Stahl und Eisen, 1942, vol. 62, Mar. 26, pp. 269–270). In the preparation of basic Bessemer converter bottoms the refractory mass is rammed round the pins projecting upwards from a steel plate which forms the base-plate of a press; the ram of the press carries another plate with holes in it which register with the pins. On withdrawing the base-plate, the holes left by the pins form the tuyères. In this paper the author shows how to determine the number, diameter and distribution of the pins in order to obtain a uniform distribution of the blast over the converter bottom.

**Advancements in the Manufacture of Open-Hearth Steel.** W. J. Reagan. (Blast Furnace and Steel Plant, 1942, vol. 30, Jan., pp. 48–51, 71; Feb., pp. 227–232). The author discusses improvements in steelmaking practice which are now receiving attention in the United States. The dephosphorisation of steel in the launder between the acid Bessemer converter and the ladle with a flux consisting of impure lime 50%, dried mill-scale 30% and fluorspar 20% is referred to; this reduced the phosphorus in two cases from 0.147% and 0.192% to 0.060% and 0.076%, respectively. The dephosphorised Bessemer steel is suitable for the production of galvanised steel sheets. Reference is made to the deterioration in the quality of steel scrap now available, the casting of a 230-ton ingot from two open-hearth furnaces, the reduction in the number of standard specifications for carbon and alloy steels, and to the

installation of a cupola to provide additional hot metal for a Bessemer plant, so as to keep the converters working for long periods. Too much light scrap and too slow charging have led to larger size of charging-box for open-hearth furnaces and has stimulated the use of partly blown metal. Other points discussed include: automatic control equipment for air, gas, furnace pressure and furnace roof temperature; rapid methods of analysis; manganese and chromium conservation; deoxidation practice; bath-temperature measurement and slag control.

**Standard Costs for Fuel in Open-Hearth Furnaces.** F. Ryder. (Blast Furnace and Steel Plant, 1941, vol. 29, Oct., pp. 1115-1118; Nov., pp. 1112-1115; Dec., pp. 1210-1212). The author makes numerous references to the literature on costing for the open-hearth process, and discusses how factors such as the quality of steel being produced, the quality of scrap, the proportion of pig iron and scrap in the charge can be defined and determined, and the effects of the shape, size and composition of the material in the furnace on the fuel consumption.

**Experience in the Production of Free-Cutting Steels.** S. Afanas'ev. (Stal, 1940, No. 10, pp. 24-25). (In Russian). Bessemer steels with carbon, 0.08-0.15%, manganese 0.60-0.90%, silicon 0.15-0.30%, sulphur 0.075-0.15% and phosphorus 0.080-0.150% were produced. After some preliminary tests it was found advantageous to use low-carbon silico-manganese for preliminary and final deoxidation of the metal. Phosphorus was added as 27% ferro-phosphorus. Sulphur was added in the ladle while pouring the metal from the converter. Loss of sulphur amounted to 35-45%. The tendency of the corners of the ingots and blooms to develop cracks was eliminated by pouring the metal into hot-top, wide-end-up moulds. Metal should be poured from the converter at 1520-1500° C. and poured into the moulds at 1440-1460° C. Hairline cracks in blooms could be reduced by increasing the amount of aluminium added in the ladle, or completely eliminated by bottom-pouring. The mechanical properties of the steels are reported.

**Trends in Steel Manufacture.** G. A. V. Russell. (Cleveland Institution of Engineers: Iron and Coal Trades Review, 1942, vol. 144, Feb. 20, pp. 165-166; Feb. 27, pp. 192-193). The author contrasts good practice in steel manufacture in the period 1919-1925 with that of the period 1935-1941. In open-hearth operations the percentage of hot metal in the charge will often be determined by commercial considerations, but it is important to know the effect of the proportion of hot metal on the speed of operation. Statistics are quoted from an American works producing 200,000 tons of ingots per month, and these show that there is a progressive reduction in heat times, as the average proportion of hot metal charged is increased from 40% to 70%. In the case of 175-ton furnaces the average time for the heats was reduced from about 12 to 10 hr. The metallurgical aspect of furnace loading (*i.e.*, heat consumed per

ton of metallic charge) is, in hot-metal practice, largely determined by the effect of iron composition on slag volume, and in high-scrap practice, by the bulkiness of the scrap. A rough-and-ready index for the effect of iron composition can be obtained as follows: multiply the silicon content by 2, add the phosphorus content and divide by the reciprocal of the proportion of iron in the charge; when the figure thus obtained is more than 1.5, steps must be taken to keep the slag bulk down, if time is not to be lost. Tables are presented in which the heat requirements and costs of converting 1 ton of hot metal into steel by the basic Bessemer and open-hearth processes are compared. Progress in electric furnace technique and combined processes of steelmaking are discussed.

**The Manufacture of High-Quality, Low-Cost Steel.** P. J. McKimm. (Steel, 1942, vol. 110, Mar. 9, pp. 76-80). Continuation of a series of articles (*see* Journ. I. and S.I., 1942, No. I, p. 179 A). The author discusses how changes in melting practice resulted in a reduction in the number of rejections in the rolling mill, also methods of recarburising the bath and other points in open-hearth practice. Amorphous graphite is often used in the production of acid open-hearth steel, owing to the high cost of low-phosphorus pig iron. A good method of adding the graphite is to charge it in drums, or to bury it between layers of turnings or borings in the charging boxes. In basic steel practice it is usually added on the bottom, or between the lime charges. Observations have shown that the total time for a heat is longer with fast charging and an early addition of the hot metal than with slow charging and a late addition of hot metal, because fast charging of cold materials chills the bottom, the banks and the furnace generally.

**Desulphurisation with Manganese and Lime.** J. Görissen. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Feb., pp. 347-350). The author briefly discusses the thermodynamic basis of desulphurisation, dealing with the reactions between the bath and the slag only and ignoring the gas phase. He shows that lime, manganous oxide and magnesium oxide—the ability of which to desulphurise decreases in that order—become more active desulphurisers as the temperature increases, while the opposite applies to sodium oxide, which is the most effective desulphuriser. He then discusses desulphurising with ferrous-oxide/manganous-oxide and ferrous-oxide/manganous-oxide/silica slags, presenting desulphurisation diagrams for these two types of slag. He also reports on some work on desulphurising with acid as well as basic lime/ferrous-oxide/silica slags, and on some experiments which indicated that fluorspar does not appreciably affect the desulphurisation.

**The Influence of Some Process Factors on the Gas Content of Molten Steel.** L. Katsen and A. Bulavkin. (Stal, 1940, No. 10, pp. 16-20). (In Russian). The hydrogen content of samples taken at various stages of fifty heats in 120-150-ton basic open-



hearth furnaces was determined, and the results are discussed from the point of view of the effect of various process factors. The hydrogen content of molten steel during the melting period increased continuously, and this period should therefore be shortened by increasing the supply of heat to the furnace. The percentage of iron ore added to the molten steel plotted against the gas content of the metal at the beginning of the subsequent boil gave a curve showing least gas at between 2% and 4% ore. Bauxite added during this period should be dried. Bauxite added during the period of the boil increased the gas content. Such additions should therefore be reduced to a minimum, the requisite slag being formed in the preceding stages of the heat. During the boil, rapid elimination of the carbon and a low viscosity of the slag result in reductions of the gas content. During the subsequent deoxidation the gas content is increased by the addition of ferro-alloys; consequently the manganese content of the metal should be controlled to reduce the amount of deoxidisers required.

**Causes of Macrostructural Defects in Medium-Carbon Steel and their Elimination.** S. Lifshits. (Stal, 1940, No. 10, pp. 20-23). (In Russian). Statistical data obtained by the author indicate that the tendency to develop flakes can be substantially reduced by working at higher temperatures and securing a rate of elimination of carbon of not less than 0.003% per min. during the period of the boil after the addition of ore. Addition of moisture-containing materials—bauxite and especially lime—is undesirable, and should be kept to a minimum. Lime for slag-forming purposes should be added sparingly at an early stage during the addition of the ore. The moisture content of the lime should be checked and kept low by storing in a dry place. The cooling of metal during rolling should be slow. The "light skin" defect in bottom-poured ingots is shown to be a consequence of too low pouring temperatures and low pouring rates.

**Direct Consumption of Aluminium in the Steel Industry.** (American Iron and Steel Institute: Contributions to the Metallurgy of Steel, No. 1, 1941). This is a brief report, prepared at the request of the Office of Production Management (U.S.A.) by an informal committee of metallurgists selected from the Technical Committees of the American Iron and Steel Institute, on the proper utilisation and distribution of aluminium in the steel industry. It is stated that in the latter half of 1940 aluminium was consumed at the rate of 0.698 lb. per ton of steel ingots produced, and by June, 1941, this had been reduced to 0.562 lb. It is thought that any further marked decrease would adversely affect steel production, not only by increasing the rejections, but also by decreasing the actual production. At two different plants it was demonstrated that blooming-mill production decreased by 36% and 40%, respectively, on medium carbon steels when such steels were made to a coarse-grain specification instead of to a fine-grain one.



**Investigation of Chromium-Nickel Steel Produced from Own Scrap by a Duplex Process.** V. Gol'dman and A. Koshik. (Stal, 1940, No. 10, pp. 26-29). (In Russian). The process described was developed to make new chromium-nickel steel from medium-carbon (0.25-0.30%) and low-carbon chromium-nickel steel scrap and from chromium-nickel-tungsten scrap (4% of nickel, 1.5% of chromium and about 1.0% of tungsten and 0.16% of carbon). The charge, consisting entirely of scrap, is rapidly melted in an acid electric furnace, the carbon being eliminated and the chromium reduced during the boil. Some iron ore may be added to promote the boil. The metal is then rapidly transferred to a basic furnace, where it is refined under a lime slag. Experimental 10-ton heats gave steels with very satisfactory mechanical properties and macro-structure. Detailed examination of the non-metallic inclusions revealed the changes in them caused by the two stages of the duplex process. The content of non-metallic inclusions in the finished steel corresponded to that in alloy steels melted in the usual way in basic furnaces. This duplex process results in a saving of about 60% of ferro-chromium, 80-90% of nickel and 80-90% of ferro-tungsten in the heat.

**Converter versus Electric Furnace.** (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 66, Mar. 19, p. 181). A brief report is given of a discussion organised by the South African Branch of the Institute of British Foundrymen on the comparative merits of the converter and the electric furnace for steelmaking. The high cost of power and the installation charges for the electric furnace and the simplicity of the Tropenas converter process were referred to. The Tropenas process was very quick; a 3-ton melt could, for example, be converted in ten minutes.

**The High-Frequency Induction Furnace. Part XI. The Working of the Basic Coreless Induction Furnace.** W. Bottenberg and P. Bardenheuer. (Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1942, vol. 24, No. 2, pp. 7-22). After indicating the limits of the applicability of acid coreless induction furnaces, the authors review the literature on basic linings for these furnaces, and then report on their own investigation, in which they studied a number of ordinary and special qualities of magnesite, with and without additions and binders, with regard to their suitability as lining material for coreless induction furnaces, i.e., especially their resistance to abrupt changes in temperature and to attack by slags. After some preliminary experiments in crucibles, they used a 250-kg. coreless induction furnace for their investigation. They arrived at the following conclusions: (1) The liability to crack formation is very different in various qualities of magnesite; some special brands are only slightly sensitive to changes in temperature, whereas the ordinary ones are so sensitive that their use for these furnaces is out of the question. (2) The admixture of glass powder

causes good sintering and bonding of the magnesite mass, even at relatively low temperatures, so that the tendency to spalling becomes smaller and the resistance to mechanical stress greater. (3) The deleterious effects of the shrinkage of sintered magnesite can largely be suppressed by applying as low temperatures as possible for the first few melts. (4) Some only of the magnesites examined withstand the attack of strongly oxidising slag as obtained on melting soft steels, whereas all qualities are sufficiently resistant to the medium-oxidising slags which occur in the production of hard steels. (5) In the continuous process all mixtures are fairly resistant to deoxidising slags, whereas in the intermittent process any basic lining is completely destroyed by them. The disintegration of the mass after cooling can be counteracted, however, by a special slag-melting process, which does not affect the degree of deoxidation of the steel.

The use of magnesite bricks is briefly discussed, and suggestions regarding their arrangement in the furnace are made. For reasons connected with furnace design they are suitable for large furnaces only.

In the second part of the paper the metallurgy of the basic-lined coreless induction furnace is outlined, and details are given of several carbon and alloy steel melts produced by the authors in order to demonstrate the suitability of this furnace for refining.

In an appendix brief reference is made to the experience gained in practice during the last three years when using 600-kg. and 1200-kg. basic coreless induction furnaces for the production of various types of alloy steel.

**The High-Frequency Induction Furnace. Part XII. Attempts to Increase the Safety and Durability of the Basic Lining.** P. Bardenheuer and R. Bleckmann. (Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1942, vol. 24, No. 2, pp. 23-29). The author points out that the main reason why the coreless induction furnace with a basic lining has not become popular is the danger of perforation of the lining, which would result in the molten steel coming into contact with the cooling water and causing an explosion. The liability to perforation is due to the high thermal conductivity of basic refractories, which leads to general heating up and sintering of the relatively thin linings used. The author suggests various means of keeping the temperature of the outer zone of the lining low, so that any molten steel penetrating that far will solidify immediately and a complete penetration will not occur even with very high furnace temperatures.

If the outer zone of the lining is kept cool, it becomes possible to select the furnace lining material mainly on the basis of its resistance to slag attack, whereas formerly the spalling resistance was the primary consideration.

In the authors' experiments ordinary sintered magnesites proved to be equal to special qualities and to electrically fused magnesia with

regard to resistance to slag attack. Finally, some suggestions are made regarding the compositions of slags which are less deleterious to the lining.

**Note on Arc-Furnace Refining Slags.** N. F. Dufty. (Metal Treatment, 1942, vol. 8, Spring Issue, pp. 17-18). The author discusses the equilibria between the constituents of basic electric arc-furnace slags and between the slag and the metal. Little is known about the influence of fluorspar on silica attack, but it is probable that the fluorspar decomposes with the evolution of fluorine, which reacts with the silica bricks to form silicon tetrafluoride. Practical observations indicate that carbon tetrafluoride, a gas stable at high temperatures, results from the interaction of calcium carbide and fluorspar; as this will cause wastage of both materials, it is inadvisable to use slags high in fluorspar when strongly carbide conditions are required. On the other hand, if a lime-sand slag is used, adequate basicity is accompanied by loss of fluidity, the slag is unreactive, and not much sulphur is removed. It is thought best to compromise between the highly reactive lime-fluorspar slags and the less basic lime-sand slags by using a well balanced lime-fluorspar-sand mix.

**Use of "Chrom-X" in Steel-Making.** J. H. McDonald. (Metals and Alloys, 1942, vol. 15, Feb., pp. 249-253). The production of low-carbon and high-carbon "Chrom-X" as a material for adding chromium to the steel furnace bath has already been described (*see* Journ. I. and S.I., 1942, No. I., p. 12 A). In the present paper the author describes how this material has been successfully used on a commercial scale in the production of a 1%-chromium steel, a chromium spring steel, a high-carbon low-chromium steel and steels with up to 11% of chromium.

**Small Ingot Moulds for Tool Steels.** L. F. Keeley. (British Steelmaker, 1942, vol. 8, May, p. 93). Although moulds less than 6 in. square for casting tool steels are usually of the split type, the author prefers to use solid moulds for ingots down to 3 in. square. Some reasons for this and some methods of prolonging the life of small moulds are given. When casting through a tundish it is imperative that the moulds are set exactly vertical, and it is worth while using a spirit level or a plumb-line to check this.

**A Lighter-Weight Cast-Iron Mold Stool.** W. W. Bergmann. (Steel, 1942, vol. 110, Mar. 9, p. 86). The author describes and illustrates an improved design of ingot mould stool, the underside of which is ribbed instead of being flat. The centre portion is 1 in. thicker than that of the ordinary stool, but a great deal of weight—as much as 1500 lb.—is saved by having the ribs instead of the uniform thickness, and an increase in the stool life has been obtained. An all-welded ingot car is also briefly described.

**Ways of Obtaining Sound Ingots.** N. Chuyko. (Stal, 1940, No. 10, pp. 37-39). (In Russian). The partial pressures of the gases in steel (such as hydrogen, nitrogen, carbon monoxide)

increase during solidification of the ingot. To obtain completely sound ingots the total gas pressure within the steel during solidification of the ingot should not exceed the outside pressure on the metal. The partial pressures of the various gases can be calculated if their percentage contents in the metal are known. It is shown—for example, in the case of hydrogen—that even a slight increase in the hydrogen content of the metal results in an appreciable increase in the partial pressure of the hydrogen, *e.g.*, in steel with 0.002% of hydrogen, its partial pressure will reach 4.54 atmospheres during solidification, and the ingots will show porosity throughout. If the total gas pressure exceeds one atmosphere during solidification, porosity will be limited to the upper portions of the ingots, where the ferrostatic plus the atmospheric pressures are unable to balance the total pressure of the gas in the steel. The author suggests that sound ingots can be obtained by bottom pouring if sufficient ferrostatic pressure is provided during solidification, provided that the bottom of the ingots solidify last. Alternative methods are the placing of filled moulds in chambers where solidification is allowed to proceed under an air (or other gas) pressure of 2–4 atmospheres, and in the case of large ingots, the use of moulds which can be covered with air-tight lids through which the necessary compressed air can be supplied to the space in the mould above the metal.

**Equipment and Dimensions of Hydraulic Plants, Especially for Basic-Bessemer Steel Works.** H. Dittmar. (Stahl und Eisen, 1942, vol. 62, Apr. 2, pp. 287–293). The author discusses the advantages and disadvantages of the use of compressed air in hydraulic plants, and, as an example, gives a detailed description of the plant installed at the basic-Bessemer steelworks of the Heinrich-Bierwes-Hütte, dealing with questions of design as well as with working practice.

**Hydraulic Plant in Steel Works.** R. Yeadon. (Journal of the West of Scotland Iron and Steel Institute, 1942, vol. 49, Part 4, pp. 61–72). The author discusses, as far as possible in non-technical terms, the various types of hydraulic pumps used in steelworks, and some of the special problems associated with their use.

## FORGING, STAMPING AND DRAWING

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(Continued from pp. 12 A–14 A)

**Eliminating Drop-Hammer Vibrations.** G. Laidler. (Iron Age, 1942, vol. 149, Apr. 2, pp. 54–55). The author describes and illustrates the design of a new foundation block for a 13-cwt. drop-hammer dropping a maximum of 36 in. at one blow per sec. The new foundation was necessary to eliminate vibration. This was done by constructing a concrete pit with outside dimensions



16 × 14 × 12 ft., with the pit itself sufficiently large to hold a suspended concrete inertia block 9 × 9 × 10 ft. with a 2-in. clearance all round. The inertia block was made of concrete poured in a welded tank; it weighed 55 tons, and was suspended from four pairs of 12-in. channels, the ends of which rested on spring-isolator units mounted in recesses in the rim of the pit.

**Aircraft Drop Forgings.** A. H. Milnes. (Steel, 1942, vol. 110, Mar. 9, pp. 64-66, 105; Mar. 16, pp. 68-69, 117). The author compares drop-forging practice in British and American forging shops producing aircraft parts, and discusses in turn the properties of the raw material, die material and die design, directionality, effects of excessive reduction, and temperature control.

**Forging Practice at D.L. & W. Railroad Shops.** C. Cleveland. (Heat Treating and Forging, 1942, vol. 28, Feb., pp. 65-67). An illustrated description is given of the forging shop and the heating and forging practice of the Delaware, Lackawanna & Western Railroad at Scranton, Pennsylvania, where all classes of forgings for railways are made.

**Artillery Cartridge Cases Made from Steel.** H. R. Turner. (Iron Age, 1942, vol. 149, Mar. 19, pp. 54-55). The author points out the exacting requirements of the metal of which artillery shell-cases are made, and discusses the attempts made to produce steel shell cases. By employing deep-drawing quality steel cold-worked and carefully annealed, it has been possible to meet these requirements, provided that the shells are used within a fairly short period of manufacture.

**Presses and Machine Tools in the Sheet-Metal Industry, with particular reference to Operation by Hydraulic Means.** H. C. Town. (Sheet Metal Industries, 1942, vol. 16, Feb., pp. 203-207; Mar., pp. 341-345, 358; Apr., pp. 481-485, 488). After comparing the advantages and limitations of crank or toggle-type presses with those of high-speed hydraulic presses, the author discusses recent developments in hydraulic pressure-control methods, and then describes hydraulic-press cushions, high-speed compact high-pressure pumps for oil, large high-speed hydraulic presses used in the American aircraft and automobile industry and the introduction of hydraulic drives for lathe headstock motions, as well as for operating die-making machines which duplicate wooden patterns.

**Evaluation of the Drawability of Thin Metals.** T. F. Mika. (Metal Progress, 1942, vol 41, Feb., pp. 192-197). The author describes a practical method of evaluating the drawability of metal sheet of thickness in the range 0.0075-0.015 in. Three sets of dies are required for this test. The specimen measures about 6 × 6 in. The first set of dies produces a blank with a series of ten holes with diameters ranging from  $\frac{5}{16}$  in. to  $\frac{7}{8}$  in.; the second set draws the metal at the circumference, the dies being made so that the severity of the draw varies at each hole, thus giving ten degrees of



severity; the third set of dies closes the lips of the holes over a filler plate of asbestos millboard, thus producing a form of gasket. By examining the metal after the three operations, its drawability can be determined by noting at which hole, and thus at what severity of draw, cracks first appear. The results are given of some tests on 0.010-in. sheet of Armco iron, various steels, copper and aluminium.

## ROLLING-MILL PRACTICE

(Continued from pp. 14 A-16 A)

**The Rolling of Free-Cutting Steel.** K. Akimov. (Stal, 1940, No. 10, pp. 35-36). (In Russian). Both Bessemer and open-hearth ingots of free-cutting (sulphur-containing) steel were rolled down to  $170 \times 180$  mm. blooms and subsequently to square billets, and then round to rod 43 mm. in diameter. Preheating of the ingots and soaking times did not appear to be in any way critical as regards the subsequent behaviour of the steel during rolling. Open-hearth steel rolled better than the Bessemer steel. Ingots cast from rimming Bessemer steel were completely unsatisfactory. Defects developing in the rolled material mainly took the form of cracks and tears.

**Flattening Sheets and Strip by Roller Levelling.** F. W. Robertson. (Steel, 1942, vol. 110, Mar. 16, pp. 84-90, 109-110). To meet the standard of flatness now required in certain classes of steel sheet, improved roller levelling machines have been designed. The author describes a new design of leveller in which the working rolls are of very small diameter and are supported by several groups of narrow large-diameter backing-rollers. These groups of backing-rollers can be individually adjusted in the vertical plane, and in this way unequal pressures can be applied along the length of the working rolls; this enables sheets with "full" or "short" centres to be properly flattened.

**The Design of Wide Strip Mills.** H. P. Lemm. (Stahl und Eisen, 1942, vol. 62, Mar. 26, pp. 257-265). The author considers the factors which govern the selection of a particular type of wide strip mill, and discusses and compares the performance of continuous and semi-continuous mills with five or six finishing stands, a Steckel mill, four- and five-stand Röchling mills (see p. 14 A) and a semi-continuous mill with a coil reheating furnace and five finishing stands.

**Maintaining Constant Speed and Tension in Strip-Reeling.** E. S. Murrah. (Steel, 1942, vol. 110, Mar. 30, pp. 78-80). The author describes the electrical control devices and circuits for controlling the speed of motors driving reels for steel strip, with particular reference to a machine with two reels so arranged that the

strip can be wound from one to the other and back again, the linear speed and tension being kept constant.

**The Torque of Individually Driven Rolls in Roll-Tables.** K. Backhaus. (*Archiv für das Eisenhüttenwesen*, 1942, vol. 15, Feb., pp. 351-355). The author discusses the possibilities for the application of individually driven rolls in roll-tables and develops formulæ for calculating the acceleration and torque required. The energy distribution in rolls transmitting the acceleration is discussed and presented graphically, and it is pointed out that the minimum time of acceleration of a bloom depends on the torque of the individually driven roll, the friction between the bloom and the roll, and, in certain cases, on the control of the roll-table.

## PYROMETRY

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**Commercial Pyrometry.** A. Linford and A. E. Hutson. (*Iron and Steel*, 1941, vol. 15, Dec., pp. 137-140; 1942, Jan., pp. 163-165; Apr., pp. 251-254; May, p. 282). The authors explain the theory of electrical resistance thermometers and of thermocouple pyrometers, describe the construction of thermocouple elements, insulators, sheaths and heads and discuss different circuits, giving details of the mechanism of the instruments used for indicating and recording temperatures.

**Intercomparison of Platinum Resistance Thermometers between  $-190^{\circ}$  and  $445^{\circ}$  C.** H. J. Hoge and F. C. Brickwedde. (*Journal of Research of the National Bureau of Standards*, 1942, vol. 28, Feb., pp. 217-240). The authors calibrated eight platinum-resistance thermometers satisfying the requirements of the international temperature scale, and compared their readings between  $-190^{\circ}$  C. and  $445^{\circ}$  C. The  $\delta$  values of the Callendar-Van Dusen equations for seven of the thermometers ranged from 1.49375 to 1.49862, whereas the  $\delta$  value of the eighth thermometer was 1.51155. After the effects of relative calibration errors had been minimised, the maximum differences between the readings of the seven thermometers with similar  $\delta$  values were  $0.007^{\circ}$  C. between  $-190^{\circ}$  C. and  $0^{\circ}$  C., and  $0.0013^{\circ}$  C. between  $0^{\circ}$  C. and  $100^{\circ}$  C., the maximum differences from the mean values being  $0.0040^{\circ}$  C. and  $0.0008^{\circ}$  C., respectively. The deviations of the eighth thermometer from the mean of the other seven were  $0.015^{\circ}$  C. at  $-110^{\circ}$  C. and  $0.003^{\circ}$  C. at  $+50^{\circ}$  C. Differences between readings of platinum resistance thermometers arising from assumed calibration errors were calculated by the authors and listed in tables.

## HEAT TREATMENT

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(Continued from pp. 16 A-19 A)

**New Electric Furnaces for Heat Treating.** C. L. Ipsen. (Steel, 1942, vol. 110, Mar. 30, pp. 66-68 : Heat Treating and Forging, 1942, vol. 28, Jan., pp. 94-96). The author describes and illustrates some new types of electric heat-treatment furnaces for munitions and aircraft parts. Of particular interest is an installation of vertical cylindrical furnaces for hardening, an oil-quenching tank, a vertical tempering furnace, a high-speed hoist, a transfer hood and controlled atmosphere equipment. Thin-walled tubular parts for aircraft landing gear are treated in this plant.

**Small Radiant Cups Direct Heat to Work.** F. O. Hess. (Metal Progress, 1942, vol. 41, Feb., pp. 217-220). The author describes a new design of burner for gas-fired heat-treatment furnaces. In this burner the gas-air mixture is fed to radial slots at the base of a "radiant cup"; the shape and position of the slots are such that the mixture burns in contact with the surface of the refractory cup, which is shaped to follow the natural sweep of the flames. The cup surface thus becomes highly incandescent, so that : (a) It constitutes an effective source of radiant energy of considerable area, (b) it accelerates the gas-air reaction by acting as a catalyst, and causes a very high rate of heat liberation in a small space, and (c) it ensures complete combustion before any gases pass beyond the cup into the furnace chamber. When furnaces are heated with numbers of these cups in the walls or roof, the furnace temperature can be changed very rapidly, because nearly all the heat is transmitted by radiation from the cups, and the furnace walls do not exercise the same heat-inertia effect as they do in other furnaces. The shape of the cup also causes the products of combustion to swirl back, and their velocity is thus dissipated before they pass into the furnace chamber. Successful applications of furnaces with these cup burners include the continuous annealing of strands of wire and strip, and a 72-ft. furnace for heat-treating cast tank turrets.

**Fuel Effects on Controlled Atmosphere Furnaces.** F. A. Locke. (Iron Age, 1942, vol. 149, Mar. 19, pp. 37-40). The author discusses the ability of solid, liquid and gaseous fuels when used in open-firing to change the amount of carbon in the surface of steel in reheating and heat-treating furnaces. A table is presented showing the products of complete combustion per lb. of natural gas, coke-oven gas, producer gas, bituminous coal, light oil and coke. The general atomisation characteristics of these fuels are pointed out, and the building up of scale to retard either carburisation or decarburisation is referred to.

**Heat Treating Tips.** G. B. Berlien. (Iron Age, 1942, vol. 149, Mar. 12, pp. 68-69). The author makes recommendations on

methods of selective hardening, the prevention of soft spots and distortion, and the tempering of various kinds of tools.

**Heat Treatment of Wire and Wire Products.** H. M. Heyn. (Wire and Wire Products, 1942 vol. 17, Feb., pp. 93-96, 123-124). The author reviews developments in the design of furnaces for the heat treatment of wire, and discusses the application of spheroidising to wire. This treatment consists usually of holding the metal at a temperature slightly above the lower critical point, cooling very slowly through the critical range, and holding at a temperature slightly below the critical; the purpose is to spheroidise the carbides into a form which will reduce the hardness and brittleness of the high carbon material, while retaining much of its strength. Temperature and combustion control have made precise control of the spheroidisation process possible. The author recommends the application of data obtained in austempering investigations to the improvement of the patenting of steel wire.

**The Selection of Case Depth in Gear Manufacture.** I. Stewart. (Mechanical World, 1942, vol. 111, May 1, pp. 385-389). After discussing the case depth required for various types of gear and the ways of producing them, the author reviews the qualities of steel suitable for case-hardened gears and possible causes of failure, especially chipping, pitting and fracture of the gear teeth.

**Cyanide Determination in Case-Hardening Salts.** (Machinery, 1942, vol. 60, Apr. 23, pp. 354-355). In order to make the most efficient use of sodium cyanide for case-hardening, it is necessary to be able to make periodic determinations of the cyanide content of the bath. A simple procedure for making this determination is described. It is based on the reaction of ammoniacal nickel chloride with free cyanide in solution to form a colourless sodium-nickel complex. When all the free cyanide has been used, the addition of more ammoniacal nickel chloride will tend to colour the solution bluish-green. In the procedure described dimethylglyoxime is used as an indicator to give a more definite end point.

**Gas-Hardening of Rail Ends.** Yu. Grdina and N. Shubina. (Stal, 1940, No. 10, pp. 40-44). (In Russian). Following some preliminary work in 1937, the authors have now developed an improved type of automatically operated apparatus for flame-hardening rails. Coke-oven gas at one atmosphere pressure is supplied from a compressor, together with oxygen, to a special burner. The burner, 60 × 220 mm., has six rows of openings 1.2 mm. in dia., the total number of openings being 104. The spraying head has seven water-spray nozzles. The burner and the spray-head are mounted on counterbalanced levers operated by electro-magnets, which swing them one after the other in front of the rail-head. The operation of the electromagnets is controlled by a time relay. Heating is continued for two minutes, and is followed by water spraying for fifteen seconds. The heat penetrates to a depth of 15 mm., a quenched sorbitic structure being obtained to a depth of



about 7 mm. and over a length of 200 mm. The Brinell hardness is 360–380. It is suggested that more uniform results could be obtained by using a mist rather than a spray for quenching. Gas consumption per rail end was 0.556 cu. m. of coke-oven gas (calorific value 4,000 cal. kg.) and the same volume of oxygen, with 4.7 litres of water for quenching.

**Dry Cyaniding or Nitro-Cementation.** I. Stewart. (Mechanical World, 1942, vol. 111, May 8, pp. 413–415). The author outlines the principles underlying the dry-cyaniding, or nitro-cementation, process and reviews some recent publications on it. In conclusion he discusses the possibilities of the application of the process.

**Nicarb Process of Case-Hardening.** J. F. Wyzalek and M. H. Folkner. (Heat Treating and Forging, 1942, vol. 28, Jan., pp. 39–42; Feb., pp. 89–90, 93). The authors describe the Nicarb case-hardening process and its advantages. In early experimental work successful case-hardening was obtained by using gas-flows of 11 cu. ft. of propane, 65 cu. ft. of ammonia and 35 cu. ft. of air per hr. at a maximum initial work temperature of 1600° F., the work being immediately cooled within the effective heating chamber to a temperature of about 1300° F. A comparison is made between parts of the same steel case-hardened in a cyanide bath and by the Nicarb process. At a depth of 0.004 in., the cyanide and Nicarb cases contained carbon 0.75% and 0.53%, and nitrogen 0.83% and 1.41%, respectively, and at a depth of 0.016 in. the carbon was 0.20% and 0.19%, and the nitrogen 0.04% and 0.06%, respectively. Some Nicarb installations consisting of shaker hearth furnaces, rotating cylindrical retorts and bell-type furnaces are described and illustrated.

**The Nitriding of High-Speed Steel.** I. Stewart. (Mechanical World, 1942, vol. 111, Apr. 24, pp. 359–360). The author discusses in an elementary way the hardening of high-speed steel in cyanide baths.

**Mass Production of Nitrided Tank Parts.** R. G. Guthrie. (Heat Treating and Forging, 1942, vol. 28, Feb., p. 91). A brief description is given of the equipment at an American foundry for nitriding batches of 10,000 tank track-pins at a time. These pins are  $9\frac{1}{2}$  in. long  $\times$   $\frac{3}{4}$  in. in dia., and are of a chromium-molybdenum steel. They are first heat-treated and tempered, and are then packed in five tiers of 2000 each on a circular alloy steel grid and lowered into an alloy steel retort 38 in. in dia.  $\times$  54 in. deep, supplied with cracked ammonia gas. A case depth of 0.025–0.030 in. is obtained.

**The Testing of the Scaling Resistance of Alloy Steels.** G. Bandel and K. E. Volk. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Feb., pp. 369–378). The authors discuss the possibilities for the standardisation of tests on the scaling resistance of heat-resistant steels. They discuss numerous testing methods described in the literature with regard to their suitability for routine work, and arrive at the conclusion that a method based on the determination



of the loss in weight would be best as a standard scaling test. They discuss suitable shapes and surface treatments of the specimens, the mode of exposure, the design of the furnaces used for testing in various gaseous atmospheres and in salt and metal baths, the heating period and the mode of intermediate cooling, and the technique of the removal of the scale. They consider the use of specimens  $5 \times 25 \times 50$  mm. in size desirable, and these should be annealed for 120 hr. with an intermediate cooling each day. For descaling they recommend the ammonium citrate method and, for special cases, the potassium-cyanide/soda method. The losses in weight are given in grammes per hour per square metre. The errors are as a rule within  $\pm 0.15$  g. per hr. per sq. m. The reproducibility of the results is discussed as well as the possibility of their extrapolation to long heating periods and of the determination of a maximum temperature to which the steels may be exposed in practice.

**The Bright Annealing of Mild Steel.** I. Jenkins and S. V. Williams. (G.E.C. Journal, 1942, vol. 12, Feb., pp. 38-50). The authors discuss the bright annealing of mild steel in atmospheres prepared from ammonia and from town's gas. The introduction of regenerators has reduced the effective cost of cracked ammonia atmospheres to an economic level for fairly large installations. Great attention is now being given to the application of hydrocarbon derivatives. Partly burnt town's gas contains carbon dioxide, carbon monoxide, hydrogen, nitrogen and water vapour, the proportions of which have to be controlled within certain limits for bright annealing. The theoretical aspect of these limits is dealt with at length, gas-steel and inter-gas reactions being considered in turn. The following composition of burnt town's gas is recommended for bright annealing mild steel at about  $700^{\circ}\text{C}$ .: Carbon dioxide 3.5-5.5%, carbon monoxide 10.5-8.5%, hydrogen 15.0-10.0%, water vapour  $< 2.5\%$ , oxygen nil, methane  $< 0.5\%$  and remainder nitrogen. Town's gas burners with 300 and 1000 cu. ft. per hr. capacities and horizontal and vertical electrically heated annealing installations are described in detail.

**Flame Preheating and Stress Relieving Arc-Welded High-Pressure Pipe Lines.** P. T. Onderdonk and W. Peterson. (Welding Journal, 1942, vol. 21, Feb., pp. 96-101). The authors describe a form of furnace or heating jacket which was designed for the preheating and stress-relieving of welded joints in large steam mains operating at  $950^{\circ}\text{F}$ . and 1500 lb. per sq. in. The furnace consists of a refractory-lined welded-steel casing made in two halves to bolt up round the pipe-joint, this casing having two tangential openings opposite each other. A propane burner is inserted into each opening, and a perforated baffle plate surrounding the steam-pipe keeps the flames from impinging directly on to the latter. Data on the temperatures obtained, the heating time and the gas consumption and pressure are presented. The equipment is quite

portable for field use; is inexpensive and good results have been achieved with it.

**Die-Block Heat-Treatment.** B. Thomas. (*Metallurgia*, 1942, vol. 25, Apr., pp. 176-177). The author discusses the heat-treatment of die-blocks of nickel-chromium-molybdenum No. 5 grade steel to British Standard Specification No. 224. He suggests oil-quenching from 830° C. and tempering at 640° C. with subsequent water-quenching. The soaking temperature should in each case be determined by the size of the block and be at least 1 hr. per in. of thickness from the outside to the centre.

## WELDING AND CUTTING

(Continued from pp. 19 A-22 A)

**Behaviour of Spot-Welds under Impact.** A. M. Unger, H. A. Matis and E. P. Gruca. (*Welding Journal*, 1942, vol. 21, Feb., pp. 94-S-98-S). The authors report on an investigation of the shear and impact strengths of spot-welds joining strips of steel plate 1 in. wide. Pairs of strip of each of the following materials were lapped and joined by a single spot-weld: (a) mild steel; (b) a low-alloy high-tensile steel; (c) annealed low-tensile stainless steel; and (d) cold-rolled high-tensile stainless steel. The shear strength of welds of the same area of the four materials decreased in the order (d), (c), (b), (a), which was the same order as the tensile strength of unwelded specimens of these steels. The impact test results showed that as the spot diameter was increased a point was reached at which the impact strength of the weld suddenly increased. This abrupt rise was due to the energy absorbed in the stretching or elongation of the material. It was observed that the order of the materials according to impact strength was the reverse of that relating to shear strength.

**Metal Transfer in the Metallic Arc.** L. J. Larson. (*Welding Journal*, 1942, vol. 21, Feb., pp. 107-S-112-S). The author discusses various theories which have been published to account for the forces which transfer metal from the tip of an electrode to the work during electric welding. He describes the apparatus used to obtain photographs of the trajectories of metal particles leaving an electrode, and reproduces some of these which show trajectories with bare and coated electrodes, with straight and reversed polarity direct current, and with alternating current. The data obtained showed that the particle sizes range from about 0.003 in. to over 0.010 in. in dia., and that the velocities range from 1 to nearly 30 ft. per sec. The author's theory is that the expansion of gases in the metal at the tip of the electrode supplies the force which transfers the metal across the arc space.

**Stainless-Steel Arc-Welding Techniques.** E. W. P. Smith. (Iron Age, 1942, vol. 149, Apr. 2, pp. 57-62). The author first discusses the properties of stainless steel, explaining what is meant by ferrite and austenite; he then describes in detail, with numerous drawings, welding procedures for making different types of joints in stainless-steel sheet and plate and in stainless clad steel.

**The Effects of Welding Procedure on Joints Made in Type 304 Stainless Steel.** E. P. Auler. (Welding Journal, 1942, vol. 21, Feb., pp. 98-S-106-S). The author describes an investigation of the effect of different welding techniques on the properties of butt-welds in 18/8 stainless-steel plate. The factors studied included: (a) The angle of the V groove; (b) depositing a large number of stringer beads, *i.e.*, small beads without weaving; (c) depositing fewer beads by weaving; and (d) accelerated cooling after depositing each bead. The most successful technique was to weave the beads and to cool in air after depositing each bead. To avoid slag inclusions a 90° V groove was necessary. Carbide formation will not occur in welded 18/8 steel regardless of the welding procedure, provided that the assembly is kept reasonably cool.

**Weldability—Fusibility Tests.** W. Spraragen and G. E. Claussen. (Welding Journal, 1942, vol. 21, Feb., pp. 65-S-86-S). The authors present an extensive review of the literature to July 1939 on fusibility tests as a means of determining weldability. The literature summarised deals with the behaviour of fluid weld metal, blow holes, bubbling, spatter, surface appearance and depth of fusion. The first part of the review describes tests to evaluate the properties of weld melts. Each of the factors influencing or depending on fusibility are treated separately in later sections.

**Weldability.** H. Lawrence. (Steel, 1942, vol. 110, Mar. 9, pp. 72-75, 106). The author discusses the value of hardness readings as an indication of the weldability of a steel. He points out how the hardness of the heat-affected zone is influenced by the mass of the welded assembly, the welding speed, the thickness of the electrode and its coating, the number of beads and the current input. It is suggested that hardness values be used only as indicators of other physical properties of the joint, such as strength and ductility.

**Billet Cutting for Steel Forgings.** H. E. Rockefeller. (Welding Journal, 1942, vol. 21, Feb., pp. 83-89). Illustrated descriptions are given of portable and stationary oxy-acetylene cutting machines for cutting forging blanks from long steel bars and billets. The advantages and disadvantages of cutting right through the bar and "nicking and breaking" are discussed. With the development of multi-nozzle automatic machines it is thought that cutting right through will be the more economic method. In smaller shops, where different sizes and lengths of blank are required, the portable machine that can readily be taken to the work is the most practical.

**The Tee-Bend Test to Compare the Welding Quality of Steels.** G. A. Ellinger, A. G. Bissell and M. L. Williams (Welding Journal, 1942, vol. 21, Mar., pp. 132-S—160-S). The authors describe a form of weldability test in which plates of low-alloy high-tensile steel are fillet welded to form T sections and the arms of the T are then bent in a special jig. The results of tests at from room temperature down to  $-20^{\circ}\text{F}$ . are presented and a method of statistical analysis for the evaluation of the data is described.

## PROPERTIES AND TESTS

(Continued from pp. 25 A—34 A)

**Confusion in Testing Terms and Methods.** G. P. Lenz, jun. (Metal Progress, 1942, vol. 41, Feb., pp. 198—202). The author quotes the definitions of the A.S.T.M. and the American Navy Department for the terms "elastic limit," "proportional limit," "proof stress" and "yield strength." He describes the "offset" method of determining yield-strength from a stress-strain curve and the extension-under-load method which requires an extensometer. These two methods with the same value of deformation can give widely varying results; it is therefore necessary, when specifying a yield strength for a material, to state the method by which this shall be determined. He presents a stress-strain curve with the strain shown on an enlarged scale which demonstrates the difference between the values obtained for the above stresses for an annealed cold-drawn steel, and puts forward his own definitions for these terms.

**The Development of Maurer's Diagram for Cast Iron.** H. Uhlitzsch. (Giesserei, 1942, vol. 29, Feb. 20, pp. 58—63). The author discusses some developments in the construction and application of diagrams similar to Maurer's diagram for determining the structure and properties of cast iron from the carbon and silicon contents. (See Journ. I. and S.I., 1931, No. II., p. 552 and 1939, No. II., p. 192 A). Practical experience since the publication of the original diagram in 1924 has confirmed the general correctness of Maurer's conception. Three new diagrams have since been developed, one for dry sand castings, one for green sand castings and the third for thin-walled castings.

**Non-Destructive Testing of Metals and Alloys.** J. W. Donaldson. (Metal Treatment, 1942, vol. 8, Spring Issue, pp. 2—8). The author surveys non-destructive methods of testing metals and alloys giving the characteristics and some of the limitations of the following methods: (1) Acoustic tests with a modified stethoscope and with supersonic waves; (2) optical tests including macrographic examination, spectrographic analysis and photo-elastic stress measurement;



(3) magnetic and electrical tests ; (4) radiographic tests ; (5) static load and hydraulic tests ; and (6) hardness tests.

**Magnafluxing Procedures.** F. B. Doane and M. Mages. (Iron Age, 1942, vol. 149, Mar. 12, pp. 47-52 ; Mar. 19, pp. 56-58). The authors describe an investigation of the magnaflux method of detecting cracks in steel to establish the effects of different current strength, of alternating and direct current and of the wet and dry processes on the clearness of the indications obtained. Their conclusions were : (1) The optimum period of current flow under the conditions described was 0.5 sec. ; (2) alternating current produced the clearest indications, and full-wave rectified alternating current gave results comparable with those obtained by direct current from a battery ; and (3) the indications of sub-surface defects were more clear and accurate in the dry-powder method than in the method using a suspension of iron in oil.

**Measurement of the Mean Values of Lattice Constants and Their Utilisation for the Determination of Stress by X-Ray Examination.** H. Möller and G. Martin. (Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1942, vol. 14, No. 4, pp. 41-45). The authors point out that when measuring stresses by X-ray examination it is often desirable to be able to examine larger surfaces than is possible with ordinary back-reflection technique, and they therefore suggest moving the specimen relative to the apparatus, or *vice versa*, during the exposure, so that a larger surface area (about 500 sq. mm.) is reached by the X-rays. He reports on the results obtained in this way when examining, with vertical and oblique radiation, specimens of structural steel St37 in various states of stress.

**Recrystallisation of Boiler-Plate in Hot-Working.** M. Vratskiy. (Stal, 1940, No. 10, pp. 30-35). (In Russian). Deformation experiments were carried out with prism-shaped specimens of 0.14% carbon steel (critical points :  $Ar_3$  880° C.,  $Ar_2$  770° C., and  $Ar_1$  690° C.). Specimens were given deformations of 6-50% in a press with a rate of deformation of 1.5 mm. per sec., at temperatures of 1200° to 800° C. The grain size (ferrite) in the deformed air-cooled specimens was measured in two planes, and both the area and volume of the grains are given. The curves show that at 1200° and 1100° C. there is a decrease in grain size with deformation, fairly rapid at first (7-20% deformation), and then much smaller until it becomes practically negligible. At temperatures below 1000° C. the initial decrease in grain size is followed by a sudden rise at deformations that are higher the lower the working temperature (e.g., 23% at 700° C.). This sudden rise is followed by a decrease in grain size with deformation. It is concluded that this "step" in the grain-size curves is actually the second one, the first being located at very low degrees of deformation outside the scope of the present investigation. For the production of a fine grain the deformations used should be sufficiently above the value at which

the second step of the grain-size curve is situated at that particular temperature. It was shown that for a given deformation the final grain size is larger, the larger the original grain size of the metal, which, in turn, is larger the higher the temperature to which the metal is heated prior to hot-working. Rolling should preferably be completed at temperatures just above  $A_{r3}$ .

**Curious Features in Railway Rails and Tyres.** H. O'Neill. (Metal Treatment, 1942, vol. 8, Spring Issue, pp. 15-16, 18). In describing the investigation of unusual forms of defect in rails and steel tyres, the author refers particularly to the case of a cavity 1 in. long with a maximum width of  $\frac{5}{8}$  in., which was found in a tyre which was being re-turned. It was found that the metal surrounding this was very high in nitrogen; the exact cause could not be established.

**Calculation and Graphical Representation of the Fatigue Strength of Structural Joints.** (Welding Journal, 1942, vol. 21, Feb., pp. 87-S-93-S). This paper constitutes Report No. 2 of Committee F. on Fatigue Testing, of the Industrial Research Division of the Welding Research Committee of the Engineering Foundation. (See Journ. I. and S.I., 1941, No. II., p. 135 A for Report No. 1). The Report deals only with methods of calculating and presenting fatigue-strength data; the calculation of fatigue strength at a given number of cycles is dealt with in Part I., and the method of constructing S-N (stress/number-of-cycles) curves is discussed in Part II. Some practical examples of the application of the curves are given in three appendices.

**Hardenability of Steel.** R. M. Parke and A. J. Herzig. (Metals and Alloys, 1942, vol. 15, Feb., pp. 241-244). The authors point out that the hardenability of steels of anomalous behaviour cannot be predicted from the composition, grain size, hardening temperature and cooling rate, and consider that the degree of dendritic segregation in the original ingot should also be studied. A technique for establishing a relationship between segregation as revealed by the microscope and the hardenability of a steel is described. A sample of the steel is isothermally treated at a temperature just above or just below the level of the nose of the S-curve, and it is found that the degree of austenite transformation varies in bands; if a grid is superimposed on the photograph of the structure, the percentage of austenite transformed in a given time in each band can be determined by estimating the proportion transformed in each square. By plotting the percentage transformed in each vertical row of squares against the distance at right angles to the bands, a curve with alternate peaks and troughs is obtained. Each peak gives the percentage of transformed austenite in a low-alloy region of the heterogeneous steel, and each trough the percentage transformed in a high-alloy region for the same time-period at constant temperature. If the percentage transformed in each of the two extreme regions at constant temperature is plotted against time, a curve is obtained from which

the time required for 50% transformation in the high- and low-alloy regions can be read off; the difference between these times divided by the average time has been arbitrarily taken as the "segregation factor." Thus, a perfectly homogeneous steel would have a segregation factor of zero, whilst the factor for an extreme case of segregation would approach 2. Some examples of the application of this segregation test are given.

**Magnetostriction in Electric Sheet Steels.** F. Brailsford and R. G. Martindale. (Journal of the Institution of Electrical Engineers, 1942, vol. 89, Part I, May, pp. 225—231). An investigation into the magnetostriction of five grades of iron and silicon-iron electrical sheet materials is described. It is shown that large variations in magnetostriction occur with direction in the sheet relative to the rolling direction, and typical forms of the magnetostriction hysteresis loops observed are reproduced. A theoretical analysis of some of the results throws some light on the probable directional distribution of magnetisation in the domains constituting the material.

**Magnetostriction Phenomena.** W. D. Williams. (General Electric Review, 1942, vol. 45, Mar., pp. 161—163). The author reviews magnetostriction phenomena. These fall under two general classifications, namely: (1) The changes in physical dimensions which accompany the magnetisation of magnetic materials; and (2) the change in magnetic properties due to mechanical stresses in these materials. He briefly defines the Joule, Barrett, Guillemin, Wiedeman, Villari, Wertheim and Nagaoka-Honda effects and describes some methods by which they are measured.

**The Damping Capacity of Engineering Materials.** W. H. Hatfield, G. Stanfield and L. Rotherham. (North-East Coast Institution of Engineers and Shipbuilders, May, 1942, Preprint). The authors report on an investigation of the damping capacity of plain and alloy steels, propeller materials such as cast iron and copper-zinc alloys, nickel-iron alloys, monel metal, bronze, aluminium alloys, magnesium alloys, metallic nickel and cobalt, glass, ivory, ivorine and various bakelites. A testing apparatus was designed capable of giving results over a wide range of temperatures; this is described and illustrated. It incorporated a magnetic method of deflecting the specimen, the deflection of which was recorded optically by the reflection of a beam of light from a galvanometer lamp at two mirrors, one on the frame of the apparatus and one on the swing-bar; the light was then passed to a camera with a continuously moving 35-mm. film.

Examples were noted of both increases and decreases in damping with increase in temperature, whilst in other cases over a wide range of temperature changes in damping were comparatively slight. The truly austenitic alloys showed relatively low values of damping, whilst the stainless materials of the 13%-chromium type gave particularly high values. Low carbon steel had an intermediate value. A comparison of the results, which are presented in tables,



reveals that the values for sintered carbides, although a little higher than those for cobalt (one of the constituents of the sinter) were nevertheless of the same order of magnitude. It seems very likely that a hard chemical compound such as tungsten carbide will not have a very high damping capacity, and the cobalt may be responsible for most of the damping recorded. By the same reasoning, the cementite occurring in carbon and alloy steels may not contribute a great deal to the damping, although in this case the relative amounts of carbide and matrix are very different. The exceptionally high values of damping capacity observed in nickel at room temperature were remarkable. The crystal structure of nickel is similar to that of the alloy steel containing chromium 25% and nickel 20%, yet this alloy, unlike nickel, had a particularly low damping capacity; nickel has distinctive ferro-magnetic properties, unlike the above alloy, which is non-magnetic, and it is pointed out that other austenitic alloys which are slightly magnetic have higher damping capacities than the above alloy. From the results on cobalt, nickel and the nickel-iron alloy with 36% of nickel, it would also appear that magnetic influences are important, but beyond this it is not possible to suggest an explanation of the results obtained.

**Precision Springs.** A. V. de Forest. (Wire and Wire Products, 1942, vol. 17, Feb., pp. 97—99, 122, 123). The author discusses improvements which have taken place in the properties of wire for the manufacture of springs used in weighing machines and measuring instruments. Special reference is made to "Elinvar," an alloy containing 36% of nickel, about 10–12% of chromium and a little molybdenum and manganese; this alloy was developed by Chevenard as an alloy suitable for watch springs as the temperature coefficient of the elastic modulus is practically zero.

**The Embrittlement of High-Alloy Chromium Steels in the Temperature Range of about 500° C.** G. Bandel and W. Tofaute. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Jan., pp. 307–320). The authors studied the cause of the embrittlement frequently observed in ferritic, or mainly ferritic, high-chromium steels after long periods of annealing at about 500° C. For this purpose they produced in a high-frequency furnace experimental casts (20–50 kg.) of steels or alloys with 9–70% of chromium with the following additions: Carbon, nickel, manganese, molybdenum, silicon, aluminium, titanium and phosphorus. The specimens prepared from these casts were annealed for up to 5000 hr. at temperatures between 350° and 1100° C., in most cases between 400° and 550° C. The effects of the annealing time and temperature, of the alloy additions and of various modes of heat treatment before annealing at about 500° C. on the following items was studied: Yield point, tensile strength, elongation at fracture, reduction of area, notched-bar impact strength, hardness, bending strength, creep strength, structure, lattice parameter, corrosion resistance, magnetic saturation, coercive force, electrical resistance and specific gravity.



The results led to the following conclusions : The embrittlement after annealing at about  $500^{\circ}\text{C}$ . is due neither to the precipitation of nitride and carbide nor to that of  $\text{FeCr}$ , *i.e.*, the compound known to be the cause of the embrittlement after annealing at higher temperatures ( $600\text{--}800^{\circ}\text{C}$ .). The precipitation of another iron-chromium compound, *e.g.*,  $\text{Fe}_2\text{Cr}$  or  $\text{FeCr}_2$ , is also unlikely. It seems possible, however, that a phosphorus-containing compound, perhaps a chromium phosphide, is precipitated. A more likely explanation of the embrittlement under investigation, however, is that this, like the cold-hardening of Duralumin, is due to a state of stress originating from a complex formation, this being not so far-reaching as to lead to precipitation of  $\text{FeCr}$  as a new crystallised phase.

**Precipitation Hardening and Creep Strength of Iron-Columbium Alloys and of Steels Alloyed with Columbium.** F. Wever and W. Peter. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Feb., pp. 357–363). The author points out that in iron-columbium alloys containing more than 0.5% of columbium a columbide is formed the solubility of which increases considerably with the temperature, so that it is possible to harden iron-columbium alloys by quenching with subsequent tempering (at  $500\text{--}700^{\circ}\text{C}$ .). The creep strength and the yield point increase with the hardness, whereas the notched-bar impact strength decreases. Columbium-bearing steels, with or without further alloy additions, also have the properties characteristic of binary iron-columbium alloys, provided that their columbium content is high enough to allow of the formation of the columbide in addition to columbium carbide.

**The Effect of Columbium on the Creep Strength of Steel.** W. Peter. (Archiv für das Eisenhüttenwesen, 1942, vol. 15, Feb., pp. 364–368). The author discusses the effects of the carbon content, the quenching and tempering temperatures and the structure on the mechanical properties, especially the creep strength, of columbium-bearing steels. He points out that the quenching temperature required for the achievement of maximum creep strength can be lowered by adding about 1% of silicon. No brittle fractures were obtained in long-time (5000–6000 hr.) creep tests. By comparing the creep strengths of alloys with 1% and 2% of columbium and a variety of carbon contents, the author proved that the favourable effect of columbium is due solely to the formation of iron columbide, not to that of columbium carbide. It was thus possible to obtain good creep strength values with columbium contents of only 0.2%, provided that the carbon content was lowered at the same time. In conclusion he shows that, like carbon, sulphur has also an unfavourable effect on the creep strength of columbium-bearing steel, which is due to the formation of columbium sulphide.

**The Significance of Hydrogen in Steel and Cast Iron.** D. W. Rudorff. (Metallurgia, 1942, vol. 25, Apr., pp. 182–184). The author reviews some recent work on the effect of hydrogen in steel and cast iron, dealing especially with a paper by Houdremont and

Heller entitled "Hydrogen as Alloying Element in Steel and Cast Iron," which was abstracted previously (*see* Journ. I. and S.I., 1942, No. I., p. 68A) and included as No. 64 in the Translation Series of The Iron and Steel Institute.

**Silicon as an Alloying Element in Structural Steel St 52.** W. Mantel. (Stahl und Eisen, 1942, vol. 62, Mar. 12, pp. 222-228). The author examines the objections to using silicon as an alloying element in high-tensile steel. A quantitative evaluation of statistics on the effects of silicon, manganese, carbon, copper and phosphorus on the mechanical properties of steel reveals the superior properties of steel St 52 alloyed with silicon. A review of the literature shows that silicon has a detrimental effect on the weldability of steel, but the present author believes this to be due to old prejudices. The results of many tests on welds made on test-pieces of various steels with electrodes with different silicon contents showed that a 0.95% silicon steel is just as weldable as steel containing silicon 0.4% and manganese 1.3%.

**Use of Alloy Steels in Rock Drilling, and their Treatment.** C. G. Kemsley. (Transactions of the Canadian Institute of Mining and Metallurgy, 1942, vol. 45, pp. 154-159: Canadian Mining and Metallurgical Bulletin, 1942, No. 359). The author discusses the advantages of substituting a 1% carbon, chromium-molybdenum oil-hardening steel for the straight carbon steel generally used for rock drilling in Canada. The correct form of heat treatment for the alloy steel is given.

**Special and Alloy Steels.** W. H. Hatfield. (Metallurgia, 1942, vol. 25, Apr., pp. 163-165). The author points out how important it is, especially under war conditions, to make the best possible use of the tonnages of alloying elements available for the manufacture of steels with properties superior to those of straight carbon steels, and discusses special and alloy steels in the light of present conditions, referring in particular to those specified by British Standard Specifications 970 and 971. He directs particular attention to the economical use of the steels under discussion and to the careful salvage of their scrap.

**The Developments and Characteristics of "Substitute 66" High-Speed Steels.** A. Linley. (Metallurgia, 1942, vol. 25, Apr., pp. 179-182). After a brief review of the development of molybdenum high-speed steels, the author deals with the "Substitute 66" class of high-speed steels, which contain 5-6% of molybdenum and 5.5-6.5% of tungsten. These steels have become the most popular molybdenum high-speed steels in the United States. This is due to the fact that, in addition to the saving in tungsten, they offer the following advantages as compared to 18% tungsten steel: (1) Forging and rolling is easier and can be carried out at lower temperatures. (2) The annealed material is easier to machine. (3) The heat treatment temperatures can be kept lower. (4) They weigh less. In the second part of his paper the author outlines the

forging, annealing, hardening, quenching and tempering treatments suitable for "Substitute 66" steels.

**Ferrous Materials Used in the Construction of Enemy Aircraft.** H. Cornelius. (Stahl und Eisen, 1942, vol. 62, Mar. 5, pp. 197-206). The author surveys the results of numerous tests of the structure and properties of the steels and cast irons used in modern British, American, French and Russian military aircraft.

**Stainless Steel in Aircraft.** (Iron and Steel, 1942, vol. 15, May, pp. 261-266). Owing to a shortage in the supply of aluminium in the United States, stainless steel is finding increasing use in the construction of aircraft. In the present paper the advantages of using stainless steel are discussed; these include the ease with which it can be spot-welded and the benefits accruing from welded as compared with riveted structures, the stiffness of stainless steel sheet and its resistance to corrosion and high temperatures.

**Training Planes Built with Low Alloy Steel.** (Iron Age, 1942, vol. 149, Apr. 2, pp. 68A-68C). A brief description is given of an American aeroplane for training purposes which is now being built of low-alloy steel and plywood; in this way the amount of aluminium required has been reduced by 75% whilst the total weight of the aeroplane has been increased by only 3%.

## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 34 A-37 A)

**The Development of Metallography.** H. Morrogh. (Journal of the West of Scotland Iron and Steel Institute, 1941-42, vol. 49, Part III., pp. 43-45). The author reviews the history of the development of metallography, referring briefly to the first freezing-point diagram for iron-carbon alloys, the research which led to the construction of many equilibrium diagrams, improvements to the microscope, X-ray methods of crystal analysis and improvements in etching reagents.

**Graphite Crucibles in Wartime.** J. Desmond. (Metal Treatment, 1942, vol. 8, Spring Issue, pp. 36-37). The author makes recommendations for increasing the life of graphite crucibles. These are classified under the headings: (a) Storing; (b) use of supports and positioning the crucible in a furnace; (c) heating a new crucible; (d) precautions in melting; and (e) notes on combustion.

**A New Method for the Determination of the Surface Quality of Technical Materials.** J. Heyes and W. Lueg. (Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1942, vol. 24, No. 3, pp. 31-39). The authors describe a new method for the determination of the surface quality of flat and cylindrical specimens, the surface quality being defined as the reciprocal of the roughness. The surface to be studied is examined under the microscope with

dark-field as well as with bright-field illumination, and the light leaving the objective is measured with the aid of a photo-electric cell, the ratio of the current intensity obtained with dark-field illumination to that obtained with bright-field illumination being taken as the criterion of the surface quality. The new method can be used for the examination of rough as well as polished surfaces. The results obtained for a number of steels are reported and shown to be in good agreement with those of older methods.

**The Metallographic Differentiation of Sand, Furnace Slag and Shrinkage Defects in Cast Iron.** H. Morrogh. (Journal of the West of Scotland Iron and Steel Institute, 1941-42, vol. 49, Part III., pp. 46-47). The author discusses the characteristics of defects in cast iron due to slag in the molten metal, sand washed off the mould-face, shrinkage, and how these can be differentiated under the microscope.

**The Metallographic Recognition of Small Alloy Additions in Grey Cast Iron.** H. Morrogh. (Journal of the West of Scotland Iron and Steel Institute, 1941-42, vol. 49, Part III., pp. 49-51). The author considers to what extent the microscope can be used to detect the presence of small quantities of alloying elements in grey cast iron. Nickel, chromium and copper, where present in small amounts, are almost impossible to detect, whilst molybdenum, aluminium and titanium can be definitely detected under certain conditions.

**Sulphur Print Reproduction.** J. S. Vipond. (Iron and Steel, 1942, vol. 15, Apr., p. 229). The reproduction of a number of black and white photographic prints of sulphur prints is not considered satisfactory. In the present article the author briefly describes a method of producing coloured reproductions from original sulphur prints by toning with sodium sulphide. These are exact replicas of the original, the variation in tone and colour being practically negligible. The solutions used and the procedure are described in detail.

**Phosphorus Concentration in Steel.** (Sheet Metal Industries, 1942, vol. 16, Apr., p. 471). A description is given of a simple method of obtaining prints which reveal the distribution of phosphorus and other elements in steel which have previously been made radio-active. A disc of the steel about as big as a penny is prepared, and a piece of photographic film is placed on each side of it; these are covered with small brass plates, and the whole pack is clamped up and placed in a tin to exclude light. The exposure takes several hours, but on development the position of radio-active elements is revealed by light areas. This method has shown that phosphorus accumulates round blow-holes in steel.

**Deep Etching.** G. W. Walker. (Iron Age, 1942, vol. 149, Apr. 2, pp. 45-51). The author describes in detail the equipment, preparation of specimens and solutions, and procedure for deep-etching steel and presents many macrographs illustrating the



different types of defects revealed by this method in bars, billets, forged crankshafts, ring-gears, connecting rods, rivets and bolts.

**A Radiographic Method for the Study of the Microstructure of Iron Ores.** H. Kirchberg and H. Möller. (Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1941, vol. 23, No. 17, pp. 309-314). The author developed a radiographic method for the study of the microstructure of iron ores the only heavy metal contained in which is iron or iron with a known proportion of manganese. The darkening of a photographic plate caused by X-rays transmitted through very thin sections (about 0.030 mm.) of the ore under investigation is measured. The results are qualitative only, as it is as yet not possible to measure the thickness of the sections examined with the accuracy that would be required for quantitative work. By comparing the radiograph with an ordinary micrograph, however, valuable information on the composition of the ore and the yield to be expected from it can be gained.

**Radiograph Intensifying Screens.** A. L. Christensen and H. F. Kaiser. (Iron Age, 1942, vol. 149, Apr. 2, pp. 63-64). The authors discuss the value of different materials for making intensifying screens for preparing duplicate radiographs by single exposures using 75-225 kV. For voltages in the lower part of this range good intensifying action and mechanical properties were obtained with screens made by electroplating 0.0015 in. of silver on 0.004 in. nickel-silver sheet; this screen is faster than a lead screen and has better mechanical properties.

**Hot-Quenching of High-Speed Steel.** R. H. McCarthy. (Mechanical Engineering, 1942, vol. 64, Mar., pp. 201-204). The author describes an investigation of the transformation of austenite in 18/4/1 (tungsten/chromium/vanadium) high-speed steel on quenching from 2350° F. to various temperatures in the 1400-350° F. range. An apparatus was constructed consisting of a small electrical resistance furnace incorporating a magnetic circuit, the latter comprising two silicon transformer iron pole-pieces in line passing through a primary coil at one side of the furnace, and a secondary or pick-up coil at the other. After quenching the specimen in a lead or suitable alloy bath, it was placed between the pole-faces in the centre of the furnace which was already heated to the quenching temperature. The magnetic flux had to pass from one pole through the specimen to the other pole where it caused a current to flow in the secondary coil; the furnace was allowed to cool and the magnetic flux through the tool steel increased as more and more austenite was transformed to martensite. The magnetic flux, and hence the current in the secondary coil, were kept constant throughout the research by adjusting the current in the primary circuit. Temperature readings were taken with a thermocouple and these were plotted against the changes in the amperage of the primary current. After quenching in molten metal to 700° and 900° F., the curves showed pronounced points of maximum austenite transformation at

320° and 330° F. respectively. After quenching to 1050° F. there were three points of considerable change at 550°, 470° and 350° F. The demarcation line between these two types of transformation was at quenching temperatures somewhere between 975° and 1050° F. Increasing the quenching temperature up to 900° F. decreased the amount of austenite transformed, reduced the hardness and increased the toughness. Precipitation hardness which occurred above 975° F. increased the hardness in the as-quenched state. Lathe tests showed that there was a slight tendency to a decrease in tool life with increasing quenching temperature.

**The Shape of the Transformation Curve in Cases of Restricted Diffusion.** K. Mathieu and H. Neerfeld. (*Archiv für das Eisenhüttenwesen*, 1942, vol. 15, Feb., pp. 389-392). The authors consider the transition from an  $\alpha$  to a  $\beta$  phase on cooling, assuming that the two phases are separated by a heterogeneous range and that diffusion is possible in the  $\alpha$  state but not in the  $\beta$  state. Such conditions prevail in practice on segregation and, possibly, also in connection with certain transformations in the solid state. Transformation curves calculated for continuous and stepped cooling are reproduced and compared with curves obtained by experiment. The calculations show that the quantities transformed depend on the number of steps—a phenomenon observed in practice in connection with the austenite decomposition of nickel and manganese steels.

**The  $Ac_1$  Range in S.A.E. 2335 Steel.** H. H. Bleakney and A. W. Grosvenor. (*Transactions of the Canadian Institute of Mining and Metallurgy*, 1941, vol. 44, pp. 101-110). The authors describe an investigation of the  $Ac_1$  transformation temperature range of specimens of S.A.E. 2335 steel containing carbon 0.32% and nickel 3.5%. Dilatometer readings were taken over the 900-1318° F. range and the microstructure of quenched specimens was studied. From the evidence obtained it is suggested that the  $Ac_1$  transformation in this steel occurs over a temperature range of from about 1000° F. to about 1275° F., and that this phenomenon is generally characteristic of nickel steel. It is probable that the finely dispersed martensite particles that occur after tempering at 1150° F. or lower act somewhat in the same way as spheroidised carbides, and therefore have no significantly deleterious effect on the properties of the steel. Serious impairment of properties apparently occurs only after considerable coalescence of the austenite has taken place at about 1200° F. and higher.

**The Iron-Nickel-Aluminium Phase Diagram.** W. Dannöhl. (*Archiv für das Eisenhüttenwesen*, 1942, vol. 15, Jan., pp. 321-330). On the basis of extensive but partly contradictory data published on the iron-nickel-aluminium system, the author attempted to reconstruct the phase diagram of this system. Assuming the correctness of the equilibrium conditions as found by Köster at high temperatures and of those found by Bradley and

Taylor at temperatures below 600° C., he tried to correlate the data for high and low temperatures, which mainly involved the establishment of the equilibrium between the  $\alpha$ ,  $\alpha'$  and  $\gamma$  phases. He presents numerous sections through the ternary system, and discusses at some length the structures and heats of formation of various iron-nickel-aluminium alloys. In conclusion he points out that his results are largely in agreement with those published recently by Kiuti (*see* Journ. I. and S.I., 1941, No. 11, p. 142 A).

**Modifications in the State and the Properties of Iron-Nickel-Aluminium Magnet Alloys due to Heat Treatment.** W. Dannöhl. (*Archiv für das Eisenhüttenwesen*, 1942, vol. 15, Feb., pp. 379-387). The author considers the physico-chemical conditions of "multiple" precipitation hardening, *i.e.*, hardening due to the precipitation of several phases on cooling an alloy, a condition being that the alloy can be undercooled. He points out that special hardening effects are to be expected only if the precipitation of the various phases occurs in the same range of temperature. He then discusses, on the basis of the new phase diagram (*see* preceding abstract), the precipitation and transformation phenomena observed by himself and previous investigators when studying the technically important iron-nickel-aluminium alloys with 18-30% of nickel and 9-17% of aluminium. He considers in particular the effect of various modes of heat treatment on these phenomena, the effect of superstructure formation, and the mechanical and magnetic properties of the heat-treated alloys, pointing out that maximum coercive force can be obtained only if the cooling from high temperatures is so controlled that several precipitation processes coincide.

## CORROSION OF IRON AND STEEL

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(Continued from pp. 37 A-39 A)

**Tests on the Corrosion of Buried Ferrous Metals.** J. C. Hudson, T. A. Banfield and H. A. Holden. (*Iron and Steel Institute*, 1942, this Journal, Section I.). This is an interim report on researches on the corrosion of buried metals conducted by the Corrosion Committee. The work is intended to precede the more extensive investigation contemplated by that Committee in collaboration with the Sub-Committee on Soil Corrosion of Metals of the Committee on Soil Corrosion of Metals and Cement Products of The Institution of Civil Engineers, who during the last year have made a grant in aid of the research.

Experiments on various irons and steels buried in clay soils at Binfield near Wokingham for three years are first described. The rate of general corrosion, even in these reputedly corrosive soils, was low, about 0.0015 in. per year, and, in agreement with previous tests

in the United States, no appreciable differences were found in this rate for ordinary ferrous materials, *i.e.*, cast irons, structural steels and wrought irons. In particular, the presence of low percentages of copper and/or chromium in steel or wrought iron had no effect on their resistance to corrosion under these conditions.

Data have been obtained for the effects of depth of burial and other factors on the corrosion rate, which will be of value when arranging future tests. It is shown that the experimental error is greater in this type of test than for corrosion tests under other conditions of exposure and it is concluded that future tests should be made in triplicate at least.

Samples of soil from the exposure sites were subjected to chemical, physical and microbiological examination, but it was not found possible to correlate the results of the corrosion tests with any of the soil characteristics. Sulphate-reducing bacteria were present in appreciable numbers in all the samples except one.

Work is reported on a method of determining the relative corrosiveness of soils by following the change in the electrical resistance of buried coils of wire due to corrosion. It is demonstrated that it is practicable to determine the resistance in the soil itself and that this resistance increases proportionately to the corrosion. Although the results obtained may not be strictly representative of the behaviour of massive materials such as pipes, it is hoped that the method will prove a convenient means of comparing the corrosiveness of different soils.

The paper concludes with suggestions for a continuation of the work. It is suggested that this should mainly take the form of developing the electrical-resistance method of testing. Experiments to date have been artificially accelerated by electrolysis. It remains to be shown that the method will respond suitably to the slower changes due to corrosion under natural conditions in the soil, and to correlate determinations made in this way with the more usual loss-in-weight tests on massive specimens.

**The Rate of Film Formation on Metals.** B. Lustman. Electrochemical Society, 1942, Apr., Preprint No. 81-8). The author critically reviews the experimental results published on the rate of the formation of films (up to 2000 Å. thick) on metals, and compares them with those published on the rate of the formation of scales, *i.e.*, relatively thick layers (above 2000 Å.). He shows that the two processes of film and scale formation are fundamentally different with regard to the effect of time and temperature on the rate of formation. The growth of certain films is governed by an exponential equation, that of others by a parabolic equation. The temperature variation curves of the rate of film formation exhibit characteristic minima. The surface structure of the metal, the orientation of the underlying metal crystals, the structure of the reaction products and the magnetic state of the metal were found to affect the rate of the film growth anomalously. In conclusion the various



theories on the growth of films are discussed on the basis of these experimental findings and the inadequacies of each theory are pointed out.

**Nails from Ruins of St. Pierre.** G. H. Enzian and H. F. Beeghly. (Metal Progress, 1942, vol. 41, Feb., pp. 208-211). In 1902 there was an eruption of a volcano on the island of Martinique which totally destroyed the city of St. Pierre. Explorers of the ruins found, among other things, heavily oxidised nails stuck together in clusters. These nails have been submitted to microscopical examination and analysis at two independent laboratories, and the results of these are reported in this paper. The feature of the eruption was that there was no lava flow and the destruction was caused by the blast of hot gases and incandescent dust. The outside layer of scale on the nails was hard, dense and dull grey, the underlying layer was porous and rather shiny, beneath this a little red rust was present. The general appearance of the scale, its composition and its response to etching tests indicated that it was composed principally of magnetic iron oxide contaminated with varying amounts of volcanic ash. From the data obtained it was deduced that the nails were in contact with volcanic dust at a temperature in the neighbourhood of 1090-1260° C. for a matter of hours rather than minutes. The cause of the abnormally high nitrogen content of the remaining metal of the nails will be dealt with in a later paper.

## ANALYSIS

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**Qualitative Chemical Tests for Iron, Steel and Foundry Materials.** E. C. Pigott. (Iron and Steel, 1942, vol. 15, Mar., pp. 196-199, 202). As an approach to the actual quantitative analysis of ferrous metals of unknown character, rapid qualitative methods are required. The author has developed some rapid methods, many of which require organic reagents. In this paper the procedures for testing for most of the elements associated with iron and steel, ores, slags and refractory materials are given.

**Gas Content of Liquid Steel.** L. G. Katzen. (Zavodskaya Laboratoriya : Iron and Coal Trades Review, 1942, vol. 145, Apr. 24, pp. 10-11). The author describes an apparatus for collecting and analysing the gases evolved from 2.5-kg. samples of liquid steel, and gives the composition of the gas evolved from samples taken at different stages in the open-hearth process.

**Determination of Combined Nitrogen in Steel.** H. F. Beeghly. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Feb., pp. 137-140). The author describes a rapid and accurate method for determining the combined nitrogen in carbon steel. A standard micro-Kjeldahl unit is used. The ammonia in the distillate is determined by means of the Nessler colour reaction,

and a photo-electric spectrophotometer is used to measure the intensity of the colour. Modifications of the method are necessary for pig irons and alloy steels containing nitrogen compounds not readily soluble in acid or alkali.

**The Sensitivity of Detection by Spectrum Analysis of Alloying Elements in Steel and Iron.** O. Schliessmann. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Oct., pp. 167-174). The author describes a method of spectrum analysis using a condensed spark, and an investigation of its accuracy in determining the elements associated with steel. The secondary current at 15000 V. from a transformer was used for excitation; the porous spectral carbon electrodes were 3 mm. apart, the lower one being flat and the upper one chisel-shaped. Determinations were made of the smallest detectable amount of each element dissolved in 1 c.c. of solution by the method. With the exceptions of selenium and sulphur all of the 27 elements determined could be detected when present in amounts down to  $5 \times 10^{-5}$  g. It was observed that in most cases the sensitivity of detection was about ten times as great if there was no iron in the solution because the multilineal background of the iron spectrum interfered with the definition of the spectrum lines of the other elements. The detection of molybdenum, vanadium and tungsten was not interfered with by the presence of iron. The limits of detectability of the various elements in solid samples were also established, and are given in tables and diagrams. With carbon and phosphorus the sensitivity of detection could be increased by measuring the extreme ultra-violet lines. The method described is suitable for carbon steels and low-alloy steels, but not for high-alloy steels.

**The Spectrographic Analysis of Inclusions Containing Silicate and Alumina.** J. Heyes. (*Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1942, vol. 24, No. 1, pp. 1-6). The author slightly modified the method described by Thanheiser and Heyes (*see Journ. I. and S.I.*, 1942, No. I., p. 252 A), so as to allow of its application to the examination of non-conducting inclusions. He reports on some results obtained when studying steels with silica- and alumina-bearing inclusions and with hair-line cracks. Several of the spectrograms obtained are reproduced.

**Spectrographic Analysis of Segregates.** (*Iron and Steel*, 1942, vol. 15, Apr., pp. 241-242). An abridged account is given of the apparatus and technique for making spectrum analyses of minute inclusions in the surface of steel. This is the method described by Thanheiser and Heyes in *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1941, vol. 23, No. 3, pp. 31-39 (*see Journ. I. and S.I.*, 1942, No. I., p. 252 A).

**Spectrographic Investigation of Inclusions in Steel.** R. Wehrich and W. Schwarz. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Aug., pp. 83-86). The authors describe an improved method of spectrographic analysis for the investigation of inclusions in steel

with which defects in parts of any shape can be examined. It enables the presence of such elements as calcium, magnesium, aluminium, zirconium and titanium to be detected, and the method is sufficiently rapid to be used for routine testing and control purposes.

**The Rapid Determination of Manganese, Phosphorus, Sulphur and Silicon in Pig Iron.** H. Kempf. (Stahl und Eisen, 1942, vol. 62, Feb. 12, pp. 136-140). The author describes methods by which determinations of the manganese, phosphorus, sulphur and silicon in molten iron can be made in 9 min. for each element, including the time required for sampling. The manganese is determined by H. P. Smith's persulphate/silver-nitrate process, the phosphorus by its precipitation with ammonium molybdate, the sulphur by combustion in oxygen and the potentiometric titration of the sulphuric acid formed, and the silicon by the perchloric acid method.

**Rapid Detection of Nickel in Alloy Steel.** T. H. Williams. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Jan., pp. 72-73). The author describes an improved rapid procedure for testing steel for the presence of nickel, using dimethylglyoxime as the indicator. The improvement consists in the use of the correct acid mixture to apply to the steel so that no interfering colours are formed. The acid mixture is made up of 25 ml. of distilled water, 10 ml. of sulphuric acid sp. gr. 1.84, 10 ml. of nitric acid sp. gr. 1.42, 10 ml. of 85% phosphoric acid and 10 g. of citric acid crystals. The test is non-destructive, as only one drop of the mixture is placed on the steel.

**Rapid Photometric Determination of Silicon in Steels.** R. Weihrich and W. Schwarz. (Iron and Steel Institute, 1942, Translation Series, No. 87). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1941, vol. 14, Apr., pp. 501-503. See Journ. I. and S.I., 1942, No. I., p. 253 A.

**Colorimetry in Metallurgical Analysis.** R. W. Silverthorn and J. A. Curtis. (Metals and Alloys, 1942, vol. 15, Feb., pp. 245-248). The authors describe a rapid and accurate colorimetric method for determining manganese and chromium in iron and steel using the spectrophotometer. These two elements can be determined in the same solution of the sample, with no preliminary separations, in about 15 min. with an accuracy of about 1%.

**Mercury Cathode Method for Determining Small Amounts of Titanium and Similar Metals in Alloys.** M. H. Steinmetz. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Feb., p. 109). A drawing and some brief particulars are given of a large cell suitable for determining by the mercury-cathode method small amounts of titanium, aluminium, magnesium or vanadium present in alloys. With an average size of cell it takes 14 hr. before all the amalgam-forming elements are deposited in the mercury, whilst with the larger cell and a current of 2-3 amp. at 10 V. the time is shortened to 5 hr.

**A Study of the Polarographic Determination of Vanadium and Chromium and of the Polarometric Titration of Molybdenum in Steels.** G. Thanheiser and J. Willems. (Iron and Steel Institute, 1942, Translation Series, No. 83). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1939, vol. 13, Aug., pp. 73-83. See *Journ. I. and S.I.*, 1939, No. II., p. 362 A.

**The Quantitative Polarographic Determination of the Alloy Additions in Special Steels.** M. von Stackelberg, P. Klinger, W. Koch and E. Krath. (Iron and Steel Institute, 1942, Translation Series, No. 85). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1939, vol. 13, Dec., pp. 249-262. See *Journ. I. and S.I.*, 1940, No. I., p. 214 A.

**Sampling and Examination of Vanadium-Bearing Slags.** F. Petzold. (*Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Nov., pp. 209-218). The author reports the results of a comparative investigation by eight German laboratories of methods of sampling and analysing vanadium-bearing slags. These slags consist of a mixture of oxides and iron granules which is of a crumbly nature and has been formed at temperatures between sintering and melting. The slag can be blown in a converter to form a raw material for the production of vanadium or for alloying with steel.

**The Determination of the Sulphur Dioxide Content of the Flue Gases from the Furnaces Used for the Roasting of Siegerland Spathic Iron Ore.** K. Sandstede. (*Stahl und Eisen*, 1942, vol. 62, Apr. 9, pp. 307-311). The author developed two methods for the determination of the sulphur dioxide content of the flue gases from furnaces in which spathic ores are roasted, the first for exact and the second for routine analysis.

**Volumetric Determination of Sulfur in Coal and Coke.** S. S. Tomkins. (*Industrial and Engineering Chemistry, Analytical Edition*, 1942, vol. 14, Feb., pp. 141-145). The American Society for Testing Materials has sponsored a study of the comparative accuracy and reproducibility of the standard method of determining sulphur in coal and coke (which involves its gravimetric determination as barium sulphate), and of volumetric methods using tetrahydroxyquinone and sodium rhodizonate as indicators. In this paper the author reports and discusses the results obtained. A total of 380 determinations were made in eight well-known fuel laboratories. The procedures employed in the volumetric methods are given. The principal merit of the volumetric methods is the saving in time and cost in laboratories testing a considerable number of samples each day. The volumetric methods proved to be so accurate and reliable that they are recommended for adoption as A.S.T.M. tentative standards as alternatives to the present gravimetric methods.



## BOOK NOTICE

(Continued from pp. 39 A-40 A)

INSTITUTION OF ENGINEERS, AUSTRALIA. *Australian Standard Engineering Drawing Practice*. 8vo. pp. 187. Illustrated. Sydney, 1941: The Institution. (Price 6s.).

This volume was first published in 1926 under the title of *Mechanical Drawing Standards*, and was re-issued in 1934 as *Engineering Drawing Practice*. This new edition, which has been improved and enlarged as a result of advances in engineering drawing practice, has been endorsed as an Australian Standard by the Standards Association of Australia. As with the 1934 edition, more than one method, or alternative methods for certain features of drawing practice have been included where satisfactory, and where uniformity of practice is not prejudiced to any appreciable extent.

The number of illustrations has been increased, the majority of which being reproduced from new drawings and diagrams. Typical examples of complete drawings have been included largely for the benefit of students.

The book will prove a valuable guide to the engineering student and the junior engineer and, in the opinion of Sir Henry Barraclough, who has written a Foreword to the work, will come to be accepted as the authoritative source of reference in all matters associated with the preparation and interpretation of engineering drawings.

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## MINERAL RESOURCES

(Continued from pp. 1 A-2 A)

**Pre-Cambrian Geology and Mineral Resources of the Delaware Water Gap and Easton Quadrangles, New Jersey and Pennsylvania.** W. S. Bayley. (United States Geological Survey, 1941, Bulletin No. 920). The author gives an account of the topography, geology and mineral resources of a belt 8-10 miles wide extending from Buttzville, New Jersey, in a south-westerly direction for about 16 miles.

**Manganese Carbonate in the Batesville District, Arkansas.** H. D. Miser. (United States Geological Survey, 1941, Bulletin No. 921-A, pp. 1-12). The author gives an account of the occurrence of manganese carbonate ores in north-central Arkansas and of the extent to which they have been worked since 1849.

**Manganese Carbonate in the Batesville District, Arkansas. Minerals of the Ores.** D. F. Hewett and H. D. Miser. (United States Geological Survey, 1941, Bulletin No. 921-A, pp. 12-94). The authors describe the geology and methods of mining the manganese ores referred to in the preceding abstract.

**Tungsten Resources of the Blue Wing District, Lemhi County, Idaho.** E. Callaghan and D. M. Lemmon. (United States Geological Survey, 1941, Bulletin No. 931-A). The authors give an account of the tungsten ore deposits in Lemhi County, Idaho, which is the principal tungsten mining district of that State. So far only one mine is productive, but other areas are being actively developed.

**Chrome Ore, Its Conservation and Substitution.** (Metal Progress, 1942, vol. 41, Apr., pp. 503-506). This paper constitutes a report on the position of chrome ores in the United States, prepared by the Advisory Committee of the War Production Board. From this it is apparent that for 1942, a total of 840,000 tons of ore will be required for metallurgical, refractory and chemical purposes. Should the imports of ore be reduced, existing stocks plus home production would be sufficient to last about one year.

**The Ore Deposits of Iron and Its Alloying Elements in South America.** R. Stappenbeck. (Stahl und Eisen, 1942, vol. 62, Apr. 30, pp. 369-373). The author enumerates the more important deposits of iron, manganese, chrome, nickel, tungsten, molybdenum, vanadium, titanium, zirconium, tantalum and columbium ores and of coal in South America, dealing with each State separately. He gives details regarding the situation and extent of the deposits, the types and qualities of the ores, the present output and future possibilities.

**Japanese Coal and Iron.** (Iron and Steel, 1942, vol. 15, May 14, pp. 299-303). Some information is given on the resources and



production of ores, coal, iron and steel in Japan, Korea and Manchukuo. (*See* p. 1 A).

## ORES—MINING AND TREATMENT

(Continued from pp. 41 A–42 A)

**Concentration of Manganese Nodules from Chamberlain, S. Dak.** F. D. DeVaney, S. M. Shelton and F. D. Lamb. (United States Bureau of Mines, Manganese Investigations No. 3, 1942, Feb., Report of Investigations No. 3613). The authors study methods of removing the low-grade shale from the manganese ores known as Chamberlain nodules which are found in South Dakota. (*See* p. 41 A).

**Concentration of the Manganese-Bearing Ore from the Dobbins Mine of Cartersville, Ga.** T. L. Johnston, M. M. Fine and S. M. Shelton. (United States Bureau of Mines, Manganese Investigations No. 4, 1942, Feb., Report of Investigations No. 3608).

**Beneficiation of Manganese Wad Ores from the Chinn Property, Batesville, Ark.** S. M. Shelton, M. M. Fine and J. D. Bardill. (United States Bureau of Mines, Manganese Investigations No. 5, 1942, Feb., Report of Investigations No. 3614).

**Concentration of Manganese Ores from the Little Florida Mountains, Luna County, N. Mex.** F. D. DeVaney, M. M. Fine and S. M. Shelton. (United States Bureau of Mines, Manganese Investigations No. 6, 1942, Feb., Report of Investigations No. 3620).

**Nitrogen Dioxide Process for Recovery of Manganese from Ores.** R. S. Dean, A. L. Fox and A. E. Beck. (United States Bureau of Mines, Manganese Investigations No. 7, 1942, Mar., Report of Investigations No. 3626).

**Sintering or Nodulizing of Ferrograde Manganese Mill Products and Fine Ores for Smelting Purposes.** V. Miller, F. B. Petermann, J. A. Pike and R. G. Peterson. (United States Bureau of Mines, Manganese Investigations No. 8, 1942, Mar., Report of Investigations No. 3625).

**Concentration of the Manganiferous Iron Ore from the Armour No. 1 Mine, Ironton, Minn.** M. M. Fine, S. M. Shelton and J. B. Zadra. (United States Bureau of Mines, Manganese Investigations No. 9, 1942, Mar., Report of Investigations No. 3624).

**Concentration of the Manganese-Bearing Ore from the Interstate Manganese Co., Johnson County, Tenn.** T. L. Johnston, S. M. Shelton, M. M. Fine and W. A. Calhoun. (United States Bureau of Mines, Manganese Investigations No. 10, 1942, Mar., Report of Investigations No. 3623).

**Ore-Testing Studies of the Ore-Dressing Section, Fiscal Year, 1941.** A. L. Engel and S. M. Shelton. (United States Bureau of Mines, 1942, Mar., Report of Investigations No. 3628). This paper

constitutes a Progress Report of the Metallurgical Division of the U. S. Bureau of Mines on investigations carried out during 1941 of the amenability to concentration of manganese, vanadium, zinc, lead, mercury, strontium and titanium ores occurring in the United States.

**Heat Balances and Economics of Ore-Preparation Plants. II. Crushing, Grading and Mixing Plants.** K. Guthmann. (Stahl und Eisen, 1942, vol. 62, Apr. 30, pp. 361-368). After having previously discussed the preparation of low-grade iron ores by roasting and sintering (*see* Journ. I. and S. I., 1940, No. I., p. 65 A), the author stresses in this, the second, part of his paper the importance of adequate crushing, grading and mixing of the ores before their reduction in the blast-furnace, and he reviews the more important types of crushing, screening and mixing plants used for this purpose.

## REFRACTORY MATERIALS

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(Continued from pp. 42 A-43 A)

**Shetland Chromite as a Refractory Material.** T. R. Lynam, J. H. Chesters, T. W. Howie and A. H. Jay. (Transactions of the British Ceramic Society, 1942, vol. 41, Feb., pp. 27-45). The authors made an extensive study of the physical and chemical properties of Shetland chromite from the Island of Unst. The ore has a high silica content, but the gangue material is very refractory, and reaction with magnesia leads to a chrome-magnesite brick of high refractoriness under load and low bursting expansion in contact with iron oxide. The authors show that lime, alumina and titania have a deleterious influence on the properties of the gangue, but that certain additions of iron oxide or of iron oxide with lime raise the refractoriness under load of 80/20 gangue-magnesia mixtures. The influence of these additions on the mineralogical constitution of the product was established by means of X-rays. In conclusion the authors report that works trials in open-hearth and arc furnaces have given encouraging results, and that the use of chrome-magnesite bricks made from Shetland chromite is now considered standard practice.

**An Interesting Product of Reaction between Silica Brick and a Slag of High Lime and Iron Oxide Content.** W. Hugill. (Transactions of the British Ceramic Society, 1942, vol. 41, Feb., pp. 46-50). The author describes an apparently unknown crystalline product which was obtained, together with magnetite, as a main reaction product when a silica brick was eroded at 1400° C. by a mixture of equal parts of lime-alumina-silica slag and mill scale. The crystals, the analysis of which is given in the paper, were orthorhombic with  $\alpha = 1.92$ ,  $\beta$  about 1.95 and  $\gamma = 2.0$ . The minerals

most closely resembling the product are of the pyroxene group, and a comparison of them with the crystals under investigation is made.

**Modern Blast-Furnace Refractories.** R. E. Birch. (Eastern States Blast Furnace and Coke Oven Association : Blast Furnace and Steel Plant, 1942, vol. 30, Mar., pp. 345-350 ; Apr., pp. 437-440, 470). The author discusses progress in the manufacture of blast-furnace refractories. The advantages of the vacuum-pressed brick are enumerated and the machine with which they are made is described and illustrated. The disintegration of bricks due to the deposition of carbon around particles of iron and iron compounds is dealt with. These compounds act as catalysts for the decomposition of carbon monoxide, and a German patent has been granted on the use of copper compounds in the mix to poison the iron compounds. The author's experiments do not substantiate the claims made in this patent. Burning the bricks in reducing atmospheres converts the iron to magnetite and the iron compounds to ferrous aluminium silicates which do not act as catalysts and therefore prevent the deposition of carbon. Full-scale trials are now being made with bricks of standard blast-furnace mixes fired at temperatures above the normal, to see whether the reduced porosity, increased resistance to abrasion and improved volume stability will justify their higher cost.

**Some Observations on Malleable Furnace Refractories.** J. A. Kayser. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 874-879). The author discusses the refractories used for constructing reverberatory furnaces for making malleable cast iron. The use of super-duty fireclay bricks has given increased life to the furnace bottom. Large bricks  $9 \times 6\frac{3}{4} \times 3$  in. are laid on end with the  $6\frac{3}{4}$ -in. side longitudinal to the furnace ; they are set in separate courses, not tied in with each other, as this facilitates patching. Both insulated and ventilated furnace bottoms are giving good service, but the tendency now is to build the furnace with the bottom shell plate above floor level, leaving an air space underneath it. A simple method of recording the service of bung bricks is suggested.

**Refractories for the Electric Steel Furnace.** C. A. Brashares, (Transactions of the American Foundrymen's Association, 1942-vol. 49, June, pp. 1010-1021). The author describes some of the special refractories which are now available in the United States for lining electric steel furnaces. The advantages and limitations of each kind are dealt with and the precautions to be observed in installing them are noted.

**Thermal Conductivity of Some Industrial Materials.** E. Griffiths, R. W. Powell and M. J. Hickman. (Journal of the Institute of Fuel, 1942, vol. 15, Apr., pp. 107-120). The authors describe various types of apparatus for high-temperature thermal conductivity determinations. Data are given for refractories, insulating bricks, granular and fibrous materials, mica, carbon,

graphites and metals; the refractory materials tested included a pottery fireclay, a fine fireclay, an aluminous fireclay, sillimanite, light and heavy diatomite bricks, slag wool and insulating concrete. The effect of impurities on the conductivity of iron is shown to be less at high than at normal temperatures; the values at a particular temperature lie reasonably well on a smooth curve when the thermal conductivity is plotted against the total equivalent carbon content of the added elements. The thermal conductivity of carbon is much less than that of metals. The possibility of deriving the thermal conductivity of a metal from a knowledge of its electrical resistivity is considered.

## FUEL

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(Continued from pp. 43 A-44 A)

**Fuel Economy in the Iron and Steel Industry.** E. C. Evans. (Journal of the Institute of Fuel, 1942, vol. 15, Apr., pp. 123-125). The author gives an account of the successive steps which have been taken by the British Iron and Steel Federation to effect economies in the consumption of fuel. As to blast-furnace practice, the author, in conjunction with F. J. Bailey, developed a method of co-ordinating heat consumption in the hearth with the time of the material in the furnace (*see* Journ. I. and S.I., 1928, No. I., p. 53). These two quantities could be analysed to include most of the variables affecting blast-furnace operation, and ultimately a general curve, characteristic of all blast-furnaces, was evolved by means of which the performance of individual furnaces could be assessed. An Open-Hearth Committee has been formed and statistical methods have been developed which allow of a correlation between the heat input to the furnace and the steel produced; from this a standard of performance was established, and the quantitative effect of a number of the factors involved was determined. The work of the Rolling-Mill Committee with its sub-committees dealing with reheating furnaces, rolling-mill instruments and roll design is also briefly reviewed.

**Standard Fuel Costs for Reheating Furnaces.** F. Ryder. (Blast Furnace and Steel Plant, 1942, vol. 40, Mar., pp. 351-355, 382, 383); Apr., pp. 441-443). Continuation of a series of articles (*see* p. 43 A). The author presents a specimen of a fuel standard cost and variation statement for soaking pits, and explains how it is used to compute the standard costs at standard load and at actual load, and how adjustments are made for fuel quality and for the heat released by oxidation of the charge.



**British Standard Test Code for Coke Ovens.** (British Standards Institution, No. 999—1942). This test code is deemed to contain all the necessary data for the determination of the performance of a coke-oven plant, and of the yields and qualities of the salable products, together with a full explanation of how the necessary observations should be made.

**Determination of the Temperature in the Dinas Partition-Wall of a Coke Oven.** M. D. Tamarin. (Iron and Steel Institute, 1942, Translation Series, No. 92). This is an English translation of a paper which appeared in the Russian journal *Koks i Khimiya*, 1940, No. 9, pp. 29–33; in it the author describes a theoretical method of calculating the temperature distribution in coke-oven walls built of Dinas bricks.

**New Principles in Heating Koppers-Becker Coke Ovens.** W. C. Rueckel. (Eastern States Blast Furnace and Coke Oven Association: Blast Furnace and Steel Plant, 1942, vol. 30, Mar., pp. 331–338; Apr., pp. 431–436). The author describes developments in the heating of coke ovens. He first considers the fundamental characteristics of combustion in coke-oven flues. Studies of gas-air mixture control on full-scale models with glass flues revealed that the following design characteristics are desirable: (1) The entrance velocity of the gas and air should be approximately equal; (2) the gas and air ports should be at approximately the same height; (3) the ports should be stream-lined so as to induce lamellar flow of the gas and air in the flues; (4) the gas and air velocities should be sufficient to prevent "lazy" combustion and to reduce the formation of back eddies; and (5) approximately equal densities of the gas and air to ensure slow mixing and reduce the tendency to turbulence. The improvements in blast-furnace practice have resulted in a reduced calorific value of the blast-furnace gas, and when this is below 95 B.Th.U. per cu. ft. and the gas is used for heating coke-ovens, there is an increase in the coking time; the gas must therefore be enriched if a rapid coking rate is to be maintained. The new principle employed with Koppers-Becker ovens to decrease the rate of diffusion of coke-oven gas in air is to dilute the gas with its products of combustion. To apply this a portion of the products of combustion is drawn from the waste-gas stream at the base of the down-flow flue and aspirated through the underjet and cross-connecting ducts by energy transferred to the waste gas from the fuel gas which is under pressure. Since the combustion of coke-oven gas diluted with products of combustion results in far more uniform flue temperature over the entire length of the flue, the recirculation of waste gas will enable walls of uniform thickness throughout the heating area to be used and faster coking speeds to be attained with comparative safety. Another important advantage achieved by recirculating the waste gases is that there is no carbon deposit in the gas risers of the underjet ovens.

In experiments on the efficiency of checker bricks for regenerators

it has been observed that when air abstracts heat from regenerator brick a higher temperature difference was maintained than that between waste gas and brick on the reverse cycle of flow; this led to the development of checker bricks with narrow slots 0.5 in. wide with a very large exposed surface in relation to its volume. The improved regeneration obtained with this checker brick has resulted in the low-temperature differences at the top of the regenerator at one plant of 19° F. between air and brick, and 9° F. between waste gas and brick.

**Inert Material for Agglutinating-Value Test of Coal.** W. A. Selvig and W. H. Ode. (Fuel in Science and Practice, 1942, vol. 21, May-June, pp. 46-51). In determining the agglutinating value of coking coal, a sample of the coal is ground and mixed with a sand, and test-buttons are then carbonised under standard conditions; finally, the crushing strength of the test-buttons are determined (*see* Journ. I. and S. I., 1933, No. II., p. 513). Difficulty has been experienced in finding a suitable substance for the inert material. In this paper the authors report on their experiments with various American and Canadian sands, silicon carbide, electrode carbon, kaolin grog, fused bauxite and fused aluminium oxide. The agglutinating-value test was found to be extremely sensitive to the surface characteristics and shape of various kinds of inert material, and very different results were obtained even when using different batches of sand from the same source. Of the manufactured materials tested there was not one with sufficiently uniform characteristics to give identical results. In general, silicon carbide was the most satisfactory of the manufactured products investigated.

**Production and Uses of Pig Iron and Coke.** E. Davies and A. Collins. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 113-120). In the first part of the paper the authors describe the production of coke at the coke-ovens of the Broken Hill Proprietary, Co., Ltd., Newcastle, N.S.W., the properties of the coke and its application in the foundry. In the second part they deal with the production of pig iron at the same works, the impurities in it and their effect on castings.

**Density and Porosity of Carbonaceous Materials.** R. C. Smith, jun., and H. C. Howard. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 34, Apr., pp. 438-441). The authors describe the apparatus employed for determining the densities of a number of experimental and commercial cokes using as filling fluids helium, water and mercury. The values found with helium varied with the temperature at which the coke was made and were only slightly affected by the heating rate during carbonisation. The majority of American commercial high-temperature cokes gave density values with helium of between 1.95 and 2.00. The values found in mercury were in all cases lower than those determined with helium. The porosities, calculated from the differences in density in mercury and in helium, ranged from 6% to 23% for the commercial high-temperature cokes.

## PRODUCTION OF IRON

(Continued from pp. 45 A-47 A)

**Use of Sinter to Increase Blast Furnace Output.** (Steel, 1942, vol. 110, May 11, pp. 107-108). Data are presented which demonstrate the advantages of increasing the proportion of sinter in the blast-furnace burden at an American iron and steel works from 10-15% up to 40-45%. It is pointed out that the production of pig iron can be increased more easily and in a shorter time at less cost by erecting a sintering plant than by building a new blast-furnace.

**Desulphurizing Pig Iron.** (Iron Age, 1942, vol. 149, Apr. 9, pp. 45-48). This is an abridged English translation of a report by W. Eichholz and G. Behrendt on small-scale and full-scale tests to examine the factors affecting the desulphurisation of basic pig iron. The original paper appeared in Stahl und Eisen, 1940, vol. 60, Aug. 1, pp. 677-683. See Journ. I. and S. I., 1941, No. II., p. 69 A.

**Investigations on "Falling" Blast-Furnace Slags.** T. W. Parker and J. F. Ryder. (Iron and Steel Institute, 1942, this Journal, Section I.). This paper constitutes a Report of the Slag Tests Panel to the Blast-Furnace Committee of the Iron and Steel Industrial Research Council. In it an investigation on methods of detecting "falling" blast-furnace slags is described (a "falling" slag is one which disintegrates on cooling). It is confirmed that the basic cause of falling is the inversion of the high-temperature crystalline form of  $2\text{CaO} \cdot \text{SiO}_2$  to the low-temperature form, with accompanying expansion. Measurement of expansion does not, however, provide an accelerated test for falling. A test, previously proposed by A. Guttman, making use of the ultra-violet lamp, tends to err on the unsafe side. Two new tests are proposed, both based on using only slag in which no  $2\text{CaO} \cdot \text{SiO}_2$  is present. One of these, suitable for slags which are cooled slowly, *e.g.*, by the "ball" method, depends on the use of an equation, introducing the analytical values for the oxide constituents, and is based on phase equilibrium in the systems, making use of the "suspended equilibrium" hypothesis. The other is a microscope test with polished specimens etched with a reagent which, in blast-furnace slags, is more or less specific for  $2\text{CaO} \cdot \text{SiO}_2$ . These two tests err slightly on the safe side.

**Problems of Blast-Furnace Slag Economy.** F. Keil. (Stahl und Eisen, 1942, vol. 62, May 14, pp. 409-414). The author outlines the technical and economic possibilities of utilising blast-furnace slag, and suggests a scheme for designating slags in accordance with their applicability for different purposes; this would render statistical recording possible. In addition, he reviews recent developments in the production and the use of blast-furnace slag products, dealing especially with foamed slag.

**Ferro-Alloys in Australia and Notes on Other Metallurgical Developments There.** F. R. Kemmer. (Electrochemical Society, Apr., 1942, Preprint No. 81-22). The author reports on the development of the production of ferro-manganese, ferro-silicon, ferro-chromium, ferro-tungsten and of tungsten steels in Australia since the outbreak of the war.

**Iron Powder and Its Sintering.** J. Libsch, R. Volterra and J. Wulff. (Metal Progress, 1942, vol. 41, Apr., pp. 528-530, 540, 550). The authors describe methods of producing iron powders for making articles by the powder metallurgy process and discuss their properties. Powder produced by reducing mill-scale consists of smooth rounded particles; those made by reducing magnetite ore are rough and require less pressure and a shorter sintering period; electrolytic iron powder is of a spongy nature and is improved by annealing in hydrogen. A comparison of density-pressure relationships of compacts of different types of iron particles of the same grain-size distribution revealed that, in the pressure range of 0-50 tons per sq. in., the order of increasing density was (1) decarburised iron, (2) iron reduced from mill-scale, (3) electrolytic iron and (4) iron reduced from magnetite. Illustrations showing the grain growth and recrystallisation of compacts of electrolytic iron powder after pressing at 33 tons per sq. in. at different temperatures are presented. Recrystallisation in particle boundaries and within particles was apparent after sintering at 1155° F.; at 1380° F. an entirely new structure was evident; the grain growth was excessive between 1515° and 1650° F. in electrolytic iron powder. The hardest compacts were made from powders of the finest grain size (passing through 325-500-mesh screens), but the best tensile strength, elongation and density resulted from mixed sizes (*e.g.*, coarse 66%, medium 17%, fine 17%). Increasing the fines above about 30% seriously affected the cold-pressing qualities.

**A Cast-Iron Boundary Post from the Middle Ages.** O. Niezoldi. (Giesserei, 1942, vol. 29, Apr. 17, pp. 136-137). A brief description is given of a cast-iron parish boundary post weighing about 1½ cwt. which was made about the year 1500.

## FOUNDRY PRACTICE

(Continued from pp. 47 A-50 A)

**Recent Developments in the Iron Foundry.** M. Eady. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 15-18). An abridged version of the author's address at the inaugural meeting of the Institute of Australian Foundrymen is presented. He discussed recent developments and gave a general description of the foundry of Ruston and Hornsby Ltd., Lincoln, which he had visited a short time previously.



**Some Points on Cupola Practice.** W. Pola. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 127-147). The author describes the construction and maintenance of cupola linings, the procedure for lighting up the bed coke, methods of controlling blast, charging, separating different grades of metal in one heat, and slagging; all as carried out at the foundry of Russell Manufacturing Co., Proprietary, Ltd.

**Cupola Operations.** D. J. Reese. (American Society for Metals: Canadian Metals and Metallurgical Industries, 1942, vol. 5, Mar., pp. 68-71). In this general discussion of cupola practice the author deals with fuel/metal and blast/metal ratios, tapping methods, the use of steel in the charge and the briquetting of cast-iron borings.

**Cupola-Melted High Duty Cast Irons.** W. W. Braidwood. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, May 14, pp. 67-71; May 21, pp. 89-94; May 28, pp. 117-120, 123). The author describes the development of a cupola practice for the production of high-duty iron. The normal practice at the foundry in question had been to use chill-cast, 3%-silicon pig iron and steel scrap. This procedure was modified with the object of eliminating the high-carbon, graphite-bearing constituents of the charge and ultimately to employ all-steel charges, supplying the necessary silicon and manganese by ferro-alloys rather than by special pig irons. Cupola charges of this type were expected to yield iron containing 2.5-3.0% of carbon and would permit the use, for castings of normal section, of silicon contents in excess of 2%, and would render variation in silicon content above 2% less able acutely to influence the structure and properties of the irons produced. The initial experimental melts gave encouraging results, tensile strengths of 20 tons per sq. in. being obtained on the 1.2-in.-dia. bar. The physical condition of the scrap steel in the cupola charge was a most important factor, the ideal type being moderately heavy in section and of hollow form. In the actual production of high-strength castings it was found best to maintain a coke-bed height of 36 in. above the tuyères. The steel scrap melts in the cupola at a level much nearer the zone of maximum temperature than does the iron and, as it does not take up carbon until melted, the carbon is derived wholly from a shallow layer of burning coke. To ensure an adequate depth of this vital coke layer, two methods were tried out: (1) The employment of really generous coke charges; and (2) the provision of extra coke in the form of separating or "sandwich" charges, as required. The second method was completely successful. For making the additions of alloying elements, briquettes bonded with cement were tried, as it was claimed that the oxidation of the alloying material is minimised by the protective action of the binder, but it was found better to charge unprotected ferro-alloys. Lump ferro-silicon is a more efficient alloying medium than briquetted ferro-silicon, or 15% silicon

pig iron, or lump calcium silicide. It was feared that the inclusion of returned high-strength iron scrap in the cupola charge would be accompanied by deterioration in the physical properties of the resultant cast iron, but the increase in carbon in the iron produced was much less than expected and the quality was satisfactorily maintained even when using up to 50% of returned scrap in the total charge.

Micrographs of specimens revealed that the size and arrangement of the graphite varied widely from extremely fine interlacing deposits distributed in a network around the grain boundaries, to relatively coarse flakes presenting no definite patterns whatsoever. This wide variation appeared to exert no dominating influence on the tensile strength, but it markedly affected the resistance to impact. The impact strength was inversely proportional to the regularity of the graphite pattern. In some specimens the graphite was present entirely in the form of very small flakes outlining the boundaries of what were originally the crystals of austenite formed in the earlier stages of the process of solidification; of the many names given to this form, the author prefers the term "reticular graphite." This form of graphite is always associated with lowered resistance to impact. Results of American research on the mechanism of the formation of graphite in grey irons are quoted. Tables and diagrams are presented giving details of the charging practice and the effects of ladle additions of carbon and ferro-silicon. For inoculation with carbon, discarded electrodes in lump, granulated and crushed form were available and ladle additions in any of these forms were entirely successful, lump form being probably the most suitable. The increase in carbon content was very small, but that in the structure was striking, and a substantial increase in the impact resistance was obtained, and the new procedure described has proved to be completely satisfactory for the production of high-duty iron castings.

**Effects of Moisture and Preheat of the Cupola Blast on Gray Cast Iron.** J. T. Eash and R. E. Smith. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 1022-1047). The authors describe their study of the effects of controlling the moisture content and of preheating the blast of a cupola on the properties of the medium carbon, 1% nickel iron which they produced. Their conclusions were: (1) The chill and the mechanical properties were consistently uniform and were only affected by changes in the carbon and silicon; (2) the temperature of the metal was the main factor controlling the melting rate and the composition and properties of the metal produced; (3) increasing the moisture decreased the metal temperature and the melting rate; the carbon, silicon and manganese recoveries decreased, and this caused an increase in the chill; (5) preheating the blast increased the temperature of the metal, increased the melting rate, decreased the coke consumption by up to 20% and decreased the manganese and silicon losses. A detailed

description of the experimental cupola and the auxiliary equipment is given.

**Recent Developments in Desulphurizing Cast Iron.** G. S. Evans. (Steel, 1942, vol. 110, May 25, pp. 82-88, 111-115). The author advocates desulphurising iron with soda ash in the launder or in the ladle in order to reduce coke consumption and increase iron production. The soda ash treatment not only reduces the sulphur but it improves the castability and helps to remove silicates and unreduced oxides. A procedure for using soda ash in the cupola has recently been developed; this consists of adding double the usual amount of limestone on the bed-coke and adding 1 lb. of fused soda ash with each 10 lb. of limestone, both on the bed and with the first two or three coke charges; with later charges the proportion of soda ash is reduced to 1 lb. with 20-40 lb. of limestone.

**Accelerating the Decomposition of Cementite. Development of an Iron for Short-Time Malleablising.** G. Brinkmann and P. Tobias. (Giesserei, 1942, vol. 29, Apr. 3, pp. 109-114). After briefly reviewing the literature on short-time processes for making malleable cast iron, the authors test the theory that it is easier to graphitise a fine-grained iron than a coarse-grained one. A fine-grained iron can be produced by mechanical, thermal, chemical and physico-chemical methods. Some trials by such methods are described, and it is shown that a fine-grained raw material produced by any of these methods can be made into good malleable iron by short treatments of 4-5 hr. The ways in which a fine-grained iron suitable for short-time malleablising can be produced include suitable working of the melt, slow pouring, using a cold green-sand mould and ladle additions of up to 0.2% of aluminium, titanium or zirconium.

**Some Impressions of British Steel Foundry Practice.** N. Hosking. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 65-79). In reviewing British steel foundry practice the author first describes items in the general organisation of a foundry, pointing out the advantages of a coloured card wall index system for keeping an up-to-date visible indicator of the progress of orders. Green and dry sand moulding, composition (or "compo") moulding, and cement moulding are discussed and particulars of arc feeding are given. Hammer blocks up to 60 tons and large roll castings lend themselves to this type of feeding, as they have only one large head; immediately after casting an electrode is put into the head which is still molten, and an arc is struck. By this means the metal is kept liquid for as long as 12 hr. in some cases in the region of the head, and it can thus feed down into the casting as it solidifies.

**Principles and Practice Involved in the Production of Steel Castings.** D. Clark. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 19-42). The author discusses the production of steel castings dealing in turn with (a) steelmaking, (b) moulding sand, (c) design, moulding and machining, (d) heat treatment, and (e) testing. Brief descriptions of steelmaking in



the electric furnace and the Tropenas converter are given, and the results of some experiments with ferro-zirconium additions are quoted. Eight foundry heats were made to the same specification, to four of which ferro-zirconium was added; the analyses and tensile test data of the eight heats are compared. There was a slight reduction in yield and ultimate strengths on the zirconium-treated heats and quite an appreciable increase in elongation and reduction of area values. In the milling of sand to mix the ingredients and coat the grains with the binder the rollers should not be so heavy that they crush or break up the grains; rubber-faced rollers are recommended. Ideal conditions for casting included having the steel in the most fluid state at the lowest possible temperature.

A series of micrographs and tables of test results on 1-in.-dia. cast-steel bars are presented to show variations in structure and physical properties obtained by submitting castings to standard annealing, normalising and quenching treatments. From these the superiority of normalising and quenching treatments is apparent in every case.

As to testing, the author's view is that tensile and bend tests are not always a reliable guide, and that all that is necessary is to take a Brinell test to assess the strength, provide annealing lugs which when broken off will disclose the fracture, indicating to the skilled observer the degree of resistance to impact, and as a final check, if necessary, an examination under the microscope.

**Side-Blow Converter in the Steel Foundries.** A. W. Gregg and F. B. Skeates. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 1101-1108). In the last twenty years the electric furnace has largely replaced the side-blown converter for producing steel for small and medium castings. At the present time, however, attention is again being given to this converter for steel foundry use. In this paper the authors discuss the factors which now contribute to the economic use of the converter; these factors include the ladle treatment of iron to remove the sulphur, the introduction of the photo-electric cell instrument for observing the converter flame, the flexibility of converter operation and the improved refractories now available for converter linings. An outline is also given of a triplex (cupola/converter/electric-furnace) method capable of supplying molten steel at a continuous rate for foundry operation.

**The Converter's Place in War Production.** A. W. Gregg. (Foundry, 1942, vol. 70, Mar., pp. 67, 159, 160; Steel, 1942, vol. 110, May 11, pp. 110-112, 125, 126). The author discusses the usefulness of the side-blown converter for assisting in the production of steel castings at foundries making munitions and armaments.

**Increasing Foundry Production with Existing Equipment.** D. J. Reese (Foundry, 1942, vol. 70, May, pp. 106, 107, 187-191). The author discusses methods of increasing the production of molten metal at iron and steel foundries with special reference to the



advantages of duplexing by refining cupola iron in small converters.

**Titanium Deoxidised Steel Shows Good Sulphide Distribution.** (Foundry, 1942, vol. 70, Apr., pp. 135-136, 204, 205). Some experiments are described the object of which was to determine whether additions of both aluminium and ferro-carbon-titanium could be successfully used to deoxidise steel cast in green sand moulds and prevent pin-hole porosity. The steel was melted in a small induction furnace, and after deoxidation with high-carbon ferro-manganese and 50% ferro-silicon, various amounts of aluminium (up to 3 lb. per ton) and of ferro-carbon-titanium (up to 10 lb. per ton) were added. The results showed that the distribution of sulphides was satisfactory in untreated steel, in steel treated with 2-3 lb. of aluminium and with 1 lb. of aluminium plus 7-10 lb. of ferro-carbon-titanium; with no aluminium the titanium treatment gave poor results.

**Cast Steel Mortar Shell.** E. Bremer. (Steel, 1942, vol. 110, Jan. 12, pp. 62-64). The author describes the casting and heat-treatment procedures developed by the Auto Specialities Manufacturing Co., a Michigan foundry, for making cast steel mortar bodies. (See Journ. I. and S.I., 1942, No. I., p. 136 A).

**Sand Testing.** H. A. Stephens. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 85-104). The author reviews methods of testing foundry sand and describes several types of testing apparatus, including the Crook elutriator, the A.F.A. (American Foundrymen's Association) standard rammer, the Dietert and Speedy types of moisture indicator, the B.C.I.R.A. (British Cast Iron Research Association) double compression core box, the A.F.A. permeability apparatus, the B.C.I.R.A. green compression strength apparatus, the Dietert universal strength-testing apparatus, A. A. Grubb's tensile strength apparatus, Ridsdale's hydraulic strength-testing apparatus, the Dietert sintering equipment and the Dietert mould hardness tester.

**The Nature of the Clay Substance in Natural Moulding Sands.** K. Endell, E. Wagner, J. Endell and H. Lehmann. (Giesserei, 1942, vol. 29, May 1, pp. 145-153; May 15, pp. 170-173). The authors report on an investigation of the properties of the clay substance in German natural moulding sands; the investigation forms an extension to the general review of published work on the hygroscopicity of clay binders (see Journ. I. and S.I., 1942, No. I., p. 87 A). The fractions below  $20\ \mu$  were examined by X-ray methods, and the quantity of exchangeable bases and the mechanism of base exchange were studied. The clay substance smaller than  $20\ \mu$  was found to consist of about 60-80% of clay minerals, principally mica-like minerals, small amounts of kaolin, 5-10% of limonite and 5-20% of very fine quartz. The shear strength of the green sand was found to increase with increasing proportions of exchangeable bases in the sand. The sintering capacity of the sand at  $1400^{\circ}\text{C}$ .

could be predicted from the quantity of flux (iron oxide, alkaline earths and alkalis) in the clay substance. The permeability of green sand could be determined fairly accurately from the proportion of wetted clay slimes smaller than 0.1 mm.

**New Materials for Patterns.** F. Barheine. (Giesserei, 1942, vol. 29, Apr. 3, pp. 117-119). The author discusses the properties of *Hartpapier* (hard paper), a material made out of paper impregnated with bakelite and submitted to high pressure while hot. It is said to be an excellent material for pattern-making. It is marketed in the form of sheets, bars and tubes in thicknesses of 0.2-100 mm.

**Blows Molding Sand into Cores.** P. Dwyer. (Foundry, 1942, vol. 70, Mar., pp. 62-64, 143-145). The author describes some of the mechanical equipment at the iron foundry of Electric Auto-Lite Co., Fostoria, Ohio, with particular reference to the core blowers. A larger blowing machine has also been installed for blowing green sand into moulds. The technique for preparing eight moulds for pistons in a flask is described.

**Green Sand Molds Dried by Infra-Red Lamps.** L. M. Duryee. (Foundry, 1942, vol. 70, Apr., pp. 134, 218-220). The author gives a brief description of equipment used for drying green sand moulds with infra-red rays from electric lamps. This consists of frames carrying twenty electric lamps with reflectors spaced 6 in. apart. The portability of the frames and the short drying time constitute the principal advantages of this method of drying.

**Strickle Moulding on a Difficult Flanged-Pipe Job.** J. H. West. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, June 4, pp. 143-145). The author describes a method of strickle moulding which was adopted at a South African foundry which was short of moulding boxes to construct a mould for a 3-in.-dia. cast-iron pipe 8 ft. long, the difficulty being that one of the flanges was at an angle of 35° to the axis of the pipe.

**Moulding and Casting a 6½-ton Crusher Shell.** C. Norbury and J. M. Stones. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, June 11, pp. 167-168). The authors describe the preparation of the mould and cores and the pouring arrangements in the making of a 6½-ton crusher casting at a South African foundry.

**Causes and Remedies for Scabs and Buckles in Gray Iron Castings.** L. E. Everett. (American Foundryman, 1942, vol. 4, Mar., pp. 8-10). The author presents illustrations of examples of scabs, buckles and rat-tail defects in grey iron castings, and classifies the possible causes under such headings as defects due to design, sand, cores, moulding practice and pouring practice.

**Effect of Ladle Inoculation on the Solidification of Gray Cast Iron.** J. T. Eash. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 887-906). The author reports on an investigation of the effects of ladle additions of silicon and nickel, separately and together, on the type of graphite formation in grey cast iron and of the relation of this type to the physical properties of

low-carbon irons. His conclusions are : (1) A definite relationship exists between the graphite structure and the physical properties of high-test cast iron. Low-carbon irons having randomly distributed graphite flakes possess high strength, whereas irons with fine dendritic graphite have inferior properties and high chill-forming characteristics. (2) Grey irons with fine dendritic graphite solidify in the metastable iron-carbide system as white irons; the eutectic carbide subsequently decomposes to form iron and graphite. (3) Ladle-inoculated grey irons, with randomly distributed flake graphite, solidify in the stable iron-graphite system. (4) The iron-graphite eutectic temperature was found to be 36–70° F. higher than the iron-carbide eutectic temperature in slowly cooled heavy-section grey iron castings.

**Some Factors Influencing the Graphitizing Behavior of Cast Iron.**

S. C. Masari and R. W. Lindsay. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 953–985). The authors investigated the effect of high melting and pouring temperatures on the graphitising behaviour of chilled castings containing total carbon 3.60% and silicon 0.55%. It was found that the depth of chill increased as the superheating temperature was raised. Also, for a given superheating temperature, the depth of chill was decreased and the mottled zone was narrowed by lowering the pouring temperature. Micrographs and chemical analyses showed that this behaviour was based on the presence or absence of graphite nuclei in the molten iron which act as starting-points for the precipitation of graphite. Nucleation by the introduction of an extraneous source of graphite was studied. This treatment markedly affects graphitisation, reducing the depth of chill and causing a sharp transition from the chilled to the grey zones.

**Notes on the Undercooling of Gray Cast Iron.** A. Boyles and C. H. Lorig. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 769–781). The authors record the results of an experiment conducted to determine the results of undercooling irons of the same composition. The experimental method and the apparatus are described. Each charge of grey iron (weighing 200 g.) was placed in a furnace held at 2700° F. It was heated for 30 min., and an addition of 0.5 g. of calcium-silicon was made and the melt held at 2700° F. for a further 2 min. The metal was then removed from the furnace, cooled in air for 20 sec. and poured. The remainder of the melt was then returned to the furnace for an additional 30 min., after which a second casting was poured. Marked differences in structure were obtained in the two castings, specimens from the first showing a much greater number of "rosettes" than specimens from the second. Cooling curves are presented for both types of casting. Castings poured 2 min. after the addition showed less undercooling and a quicker recovery of temperature after the initial dip in the curve. Castings poured 32 min. after the addition contained more fine eutectiform graphite



than those poured 2 min. after the addition; this was attributed to the influence of the total number of eutectic crystallisation centres on the rate of advance of the solid-liquid interface during the early stages of eutectic solidification.

## PRODUCTION OF STEEL

(Continued from pp. 50 A–57 A)

**The Development of the Open-Hearth Process at Witkowitz.** A. Rotter. (Iron and Steel Institute, 1942, Translation Series, No. 91). An English translation is presented of a paper which describes the extensions to plant and the development of the continuous pig-ore process since 1922 at the Witkowitz steelworks. This paper appeared originally in *Stahl und Eisen*, 1941, vol. 61, Oct. 9, pp. 929–937; Oct. 16, pp. 949–956 (*see* Journ. I. and S.I., 1942, No. I., p. 226 A).

**Control of the Basic Bessemer Process by Measurement of the Radiation of the Converter Flame.** G. Naeser and H. Krächter. (*Stahl und Eisen*, 1942, vol. 62, Apr. 23, pp. 341–347). The authors studied the radiation of the flame of a basic Bessemer converter, and for this purpose divided the spectrum into the following ranges: Red, green, blue, total visible radiation, total infra-red radiation, short-wave and long-wave infra-red, and total visible + invisible radiation. The greatest part of the energy is emitted in the infra-red range and is due to the bands of carbon monoxide and dioxide. Only towards the end of the process does the proportion of energy emitted in the visible range increase somewhat. The authors recommend, therefore, controlling the process first by measurement of the infra-red radiation and towards the end by measurement of the visible radiation. The authors' study of the visible radiation indicated that, in the curves in which the millivolts measured with a photo-electric cell are plotted against time, there is a certain point at which the melts have a definite phosphorus content. With the aid of calibration curves it is thus possible to tip the converter at the desired phosphorus content, which for the authors' melts was 0.06–0.07%. The manganese content of the melt can also be determined from the visible spectrum—with an accuracy of about 0.08%—provided that the pig iron used has always the same manganese content. The infra-red radiation indicates the silicon content and shows whether the melt is liable to become too hot, so that it can be cooled before an excessive amount of nitrogen can be taken up.

**The Manufacture of High-Quality Low-Cost Steel.** P. J. McKimm. (*Steel*, 1942, vol. 110, Apr. 13, pp. 88–93; Apr. 27, pp. 74–79). Continuation of a series of articles (*see* p. 52 A). The author discusses the working of basic open-hearth furnaces with



special reference to the charging of lime, fluorspar and ores, and methods of determining the condition of a heat from spoon and cake slag samples.

**Acid Steel Melting Practice.** B. J. Aamodt. (American Foundrymen's Association : Foundry, 1942, vol. 70, Apr., pp. 138-139, 212-214). The author defines and discusses many points in steel-melting practice for acid-lined furnaces.

**Protecting Water-Cooled Equipment on Open-Hearth Furnaces.** J. B. Luckie. (American Institute of Mining and Metallurgical Engineers : Steel, 1942, vol. 110, Jan. 12, pp. 70-72, 89). The author describes and illustrates the construction of water-cooled doors and ports for open-hearth furnaces. In these the water-pipes have a large number of studs welded to them, between which plastic chrome ore or other suitable refractory material is rammed ; these studs give additional cooling surface, and also increase the mechanical strength of the door lining. A successful alternative method of studding, which saves welding when new studs are required, is to weld nuts on to the tube surface and to screw short lengths of rod or bolts into the nuts.

**The Application of Electric Arc Type Furnaces to Metal Melting.** G. P. Tinker. (Proceedings of the Institute of Australian Foundrymen, 1939-40, vol. 1, pp. 1-14). The author describes the construction and principles of direct arc and indirect arc furnaces, and compares the costs of producing steel under Australian conditions in a 20-ton open-hearth furnace, a Tropenas converter and a 5-ton basic-lined electric furnace, as well as the costs of melting cast iron in the cupola and in a 3-ton electric furnace. The application and advantages of the direct arc furnace for producing malleable iron and melting and refining copper are also discussed.

**A Rotating Induction Furnace.** F. W. Scott and T. L. Joseph. (Metals and Alloys, 1942, vol. 15, Mar., pp. 415-419). In laboratory studies of metal-slag reactions difficulties have been experienced in preventing the slag from reacting with the crucible material. In this paper the authors describe an induction furnace assembly which consists of a vertical inductor coil 6 in. in dia. and 7 in. high which is kept stationary in an asbestos-lined chamber, and an alundum crucible mounted on a vertical spindle projecting through the base to a driving mechanism below. Above the chamber is a refractory cover with gas connections and a T-piece through which additions to the crucible can be made. When the metal has become molten and the crucible is revolved, the surface of the liquid assumes the shape of a paraboloid, into which the slag may be introduced and melted. To obtain data on the equilibrium conditions with respect to sulphur distribution in slag and molten steel, a technique for removing the slag at the existing temperature and instantly chilling it was developed. For this purpose a small graphite cup connected by tubing to a suction pump was lowered over the melt ; when the cup came in contact with, or very close to the molten slag, it was

instantly drawn into the cup and chilled. The preparation of the refractory crucibles, linings and spindles and of the slag samples is described. Other types of furnaces with rotating crucibles have been referred to previously (*see* Journ. I. and S.I., 1939, No. 1., p. 149 A).

**Planning Production in Iron and Steel Works.** R. Ricker and R. Steck. (*Stahl und Eisen*, 1942, vol. 62, May 28, pp. 449-456).

## REHEATING FURNACES

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**Modern Forging Furnaces.** A. F. Macconochie. (*Steel*, 1942, vol. 110, May 25, pp. 72-75). The author describes several types of furnaces for heating billets and other materials for forging purposes. Special attention is given to circular rotating hearth furnaces. One of this type is equipped with hand-controlled burners operating on a rich mixture of oil and city gas as well as some automatically controlled burners using gas only. The rapid combustion of the gas accelerates the vaporising, cracking and combustion of the oil fuel so that this is fully completed within the furnace.

**The Results of Economy Measures on Reheating Furnaces Heated with Long-Distance Gas.** W. Besse. (*Stahl und Eisen*, 1942, vol. 62, Feb. 19, pp. 156-160). A German works making forgings up to 80 kg. in weight for the aircraft industry changed over from coal, coke and oil fuel to long-distance gas for heating their furnaces; at first a considerable increase in the heating costs was noted. In this paper the author describes the steps taken which, in a period of 21 months, resulted in a decrease of 27% in the gas consumption and an increase of 15% in the production.

**Fuel Application in Metallurgical Heating Furnaces.** F. S. Bloom. (*Iron and Steel Engineer*, 1942, vol. 19, Feb., pp. 64-74). The author discusses the design of billet reheating furnaces, presenting diagrams of several types, including split flame fired furnaces, furnaces with one, two and three zones and sloping bottom pusher furnaces. The value of preheated air and burner design are also dealt with.

## FORGING, STAMPING AND DRAWING

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(Continued from pp. 57 A-59 A)

**Forging Practice.** J. Mueller. (*Heat Treating and Forging*, 1942, vol. 28, Mar., pp. 123-128). The author makes recommendations on the selection of die blocks, die design, die sinking, heating and trimming forgings and the maintenance of a forging shop,

giving as an example the manufacture of forged radiused pedals of 0.20% carbon steel.

**Wrought Iron and Chain Industry in South Staffordshire.** (Iron and Coal Trades Review, 1942, vol. 145, May 29, pp. 183-184; June 4, pp. 227-228; June 12, pp. 273-274). The history of the production of wrought iron in South Staffordshire is outlined, with especial reference to the chain-making industry, and in conclusion a modern chain-making works is briefly described.

**Reducing Costs of Large Drawing and Forming Dies.** C. W. Hinman. (Heat Treating and Forging, 1942, vol. 28, Mar., pp. 130-133). The author describes types of drawing and forming dies which are quite satisfactory when made of hard wood thus enabling a saving in die steels to be made. These dies are suitable for making many large drawn parts of simple shape, such as automobile fenders and large culinary ware.

**Drawing with Backward Pull.** W. Lueg. (Stahl und Eisen, 1942, vol. 62, May 21, pp. 432-439). The author discusses the theoretical basis of wire-drawing with backward pull, pointing out the analogy to rolling with backward pull. He gives a detailed review of the literature on the subject, dealing especially with American publications. In conclusion he emphasises the advantages of drawing with backward pull, which has so far not become popular in Germany.

## HEAT TREATMENT

(Continued from pp. 61 A-65 A)

**Heat-Treatment and Work-Effect on Steel.** B. Thomas. (Metallurgia, 1942, vol. 26, May, pp. 17-20). The author discusses the deleterious effects of overheating and of insufficient as well as too much working and the possibilities of their elimination by special subsequent treatment. He quotes three examples of steels which, owing to faulty treatment, originally had unsatisfactory structures, and had been rejected, but could have been rectified by special treatment, *viz.*, a 5% nickel case-hardening steel (British Standard Aircraft Steel S67), which had been overheated during heating for forging, and a low-nickel steel (British Standard Automobile Steel 5005/203), which, in one case, had been worked excessively and, in another case, overheated in ingot form.

**Recent Development in Heat-Treatment.** A. G. Robiette. (Metallurgia, 1942, vol. 26, May, pp. 23-24). The author reviews recent developments in the heat treatment of ferrous and non-ferrous alloys, dealing especially with various types of electrically heated and gas-fired furnaces which have become popular during the last four years.

**Some Recent Heat-Treatment Furnace Installations and Equipment.** W. Ashcroft. (*Metallurgia*, 1942, vol. 26, May, pp. 28-32). The author gives an illustrated description of some more recent types of furnaces for the heat treatment of ferrous and non-ferrous alloys, dealing especially with the temperature control equipment.

**Where Should Heat-Treating Heat Go?** (Steel, 1942, vol. 110, May 11, pp. 92, 108). Recommendations are made with regard to the position and shape of immersed electrodes in molten salt baths. Baths with sloping instead of vertical walls with the electrodes placed well apart will prevent any overheating.

**Salt-Bath Methods in Armament Manufacture.** H. L. Edsall. (*Industrial Heating*, 1942, vol. 9, Feb., pp. 192-196). The author describes and illustrates some immersed-electrode salt-bath furnaces for case-hardening armour-piercing bullets.

**Principles and Metallurgy of Induction Heating.** A. F. Macconochie. (Steel, 1942, vol. 110, Apr. 13, pp. 102-107). The author explains the principles of induction heating and describes the equipment required for heating and quenching to harden steel by this method. He discusses the differences in the electrical characteristics necessary for surface-hardening, more uniform heating as for forging, and for melting.

**Heat Treating Shells.** (Heat Treating and Forging, 1942, vol. 28, Mar., pp. 143-144). A brief description is given of a completely automatic heating, oil-quenching and tempering unit for shells. The hardening furnace is direct-fired, with burners on both sides directed over and under the charge; the tempering furnace is heated by convection, the hot gases being circulated by a fan of heat-resisting metal. The units are built in different widths to take from two to twelve parallel rows of shells end-to-end on rollers set in rails. The shells are loaded manually on to the charge rollers. The pusher mechanism is controlled by a time-clock set to produce the required heating cycle. Each operation of the pusher advances the charge one shell length through the unit. At the discharge end the shells pass down a chute into the oil, where jets of oil at high pressure also quench the surface of the cavity. Depending on the size of shell and the number of parallel tracks, from 40 to 200 can be heat-treated per hr.

**Gas Carburising.** I. Stewart. (*Mechanical World*, 1942, vol. 111, May 15, pp. 436-439). The author briefly reviews the development of gas carburising and shows why, from both theoretical and practical viewpoints, methane is unquestionably one of the best forms of hydrocarbon for gas carburising. The use of town gas, butane and propane is also discussed.

**The Application of Atmosphere Control to the Hardening of High-Speed Steel.** A. H. Holden. (*Metallurgia*, 1942, vol. 26, May, pp. 20-22). The author describes the equipment and operation of the hardening shop of a large firm of tool-makers using a protective atmosphere of the type governed by the Sheffield Gas Company's



patent, which is prepared by adding a certain percentage of unburnt town's gas to the dehydrated products of complete combustion of town's gas.

**Heat-Treating Methods for Deep-Well Plunger Pump Parts.** (Machinery, 1942, vol. 60, June 11, pp. 537-541). The equipment and procedure for heat-treating parts for pumps used at the bottom of deep wells and oil wells are described. Small liners are normalised in trays passed through a furnace by mechanical pushers. Plungers up to  $5\frac{3}{4}$  in. in dia. and 33-77 in. long are case-hardened by packing them with compound in a long tube of centrifugally cast heat-resisting steel. Valve seats are heated in an electric furnace to 1775-1875° F., held for 30-60 min., and quenched in oil.

**The Prevention of Coarse-Grain Cracks in Tools Made with High-Tungsten and Substitute High-Speed Tool Steels.** D. W. Rudorff. (Metallurgia, 1942, vol. 26, May, pp. 25-27). This is an abridged translation of a paper by O. Pattermann, which appeared in Stahl und Eisen, 1941, vol. 61, Dec. 25, pp. 1161-1168. See Journ. I. and S.I., 1942, No. I., p. 236 A.

## WELDING AND CUTTING

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(Continued from pp. 65 A-67 A)

**The Inspection of Welded Steel Joints in Relation to their Static Mechanical Strength.** J. Dearden. (Transactions of the Institute of Welding, 1942, vol. 5, Apr., pp. 47-54). The author describes an investigation in which butt- and fillet-welded joints varying intentionally in quality were prepared, examined by X-rays, and tested to destruction in tension. The fractures were then inspected and the visible defects correlated with the radiographs and the breaking loads. The conclusions drawn were: (1) Provided sufficient metal is deposited, metallic arc welds may contain gross internal defects and still retain an adequate static breaking load. (2) The strength of a fillet weld depends much more on the size and shape of the fillet than on the degree of penetration at the root, and the possibility of any weakening effect due to bad penetration may be avoided by depositing ample fillets; in butt welds the reinforcement normally given may serve a similar purpose. (3) Weld size cannot be measured with the precision generally associated with engineering and testing; it is therefore more reasonable to assess test welds on their breaking loads rather than on their breaking stresses, and the breaking load should be related to the width of the joint. (4) Except for pressure vessels, welds should not be rejected solely on radiographic evidence without some knowledge of the extent to which defects may prejudice their mechanical properties. The author also makes observations on the strength of open square butt joints, on the relation of all weld metal specimens to the strength of actual joints, on the

lack of root penetration which may be permitted in fillet welds, and on welding procedure control.

**Controlling the Effect of Contraction and Included Stresses in Welded Structures.** A. E. Berriman. (Transactions of the Institute of Welding, 1942, vol. 5, Apr., pp. 67-73). The author explains the nature of the contraction and the residual stresses in welded structures and gives examples from his own experience; from these he draws up the following simple rules for the guidance of welders: (1) Make allowances for contraction; (2) prepare the joint so that only the minimum of weld metal is required; (3) use means of holding the work, and thus obtain a partly fixed condition; (4) arrange the erection and welding of the parts so that they have as much freedom as possible to move in one or more directions; (5) weld first those joints that will cause the greatest contraction stresses; (6) deposit the greatest amount of weld metal in a unit of time; (7) distribute the heat as evenly as possible over the length of the joint by "step back" welding; (8) allow the heat to escape from the welded joint without employing artificial cooling; (9) never leave a joint to cool until the weld has reached a safe size or thickness; and (10) mechanical or heat treatment assists in equalising stresses and reduces residual stresses.

**Weldability.** H. Lawrence. (Steel, 1942, vol. 110, Apr., 6, pp. 78, 109-112). The author describes six types of ductility test used for assessing the weldability of steel. These are: (1) The free-bend test in which a specimen is cut transverse to the weld and bending takes place across the weld involving both the weld metal and the heat-affected zone. (2) The guided bend test introduced by the American Navy Department, in which the specimens are bent in a jig under more controlled conditions. (3) The bead bend test of Jackson and Luther, in which a bead is deposited in the direction of rolling down the middle of a plate  $7 \times 6 \times \frac{1}{2}$  in. The bead is then machined off and the surface ground smooth. The test-piece is then cut  $1\frac{1}{2}$  in. wide, with the welded zone down the centre, and tested in tension. (4) The T-bend test first described by Bissell, in which two  $\frac{1}{2}$ -in. plates are welded with two fillet welds to form a T with a table 12 in. long and a stalk 4 in. long. The two arms of the T are bent upwards. (5) The V-notch slow bend test, in which specimens are prepared with a machined notch as for Charpy impact testing, the notch being cut at the point of maximum hardness; the bending force is applied with the American Navy pattern jig used in test (2). (6) The Hess tensile-ductility test, for which three specimens are required. Multiple beads are applied to these test-pieces. First, the ductility is determined in a tensile test; secondly, tests are made parallel and transverse to the weld; and thirdly, tests are made in the as-welded and stress-relieved conditions. The advantages and limitations of these tests are briefly discussed.

**Weldability of Some Low Alloy Steels.** J. S. Vatchagandhy and G. P. Contractor. (Transactions of the Institute of Welding, 1942,

vol. 5, Apr., pp. 55-66). The authors report the results of hardness, tensile, bend and impact tests on welded specimens of eighteen low-alloy copper-chromium steels, some containing nickel and molybdenum. A single bead 3 in. long was deposited on the centre of a  $\frac{1}{2}$ -in. plate, sections were cut  $\frac{3}{16}$  in. and 1 in. from the starting-point; these positions are referred to as section 1 and section 2. Steels which have been known to crack when tested under conditions of severe mechanical restraint gave a maximum weld hardness higher than 400 D.P.H. (diamond pyramid hardness) in section 1 and 350 D.P.H. in section 2. From the impact test results it appears that there is a distinct tendency for low-alloy steels with tensile strengths of less than 36 tons per sq. in. to show Izod impact values higher than 20 ft.-lb. when tested in the heat-treated condition.

**Testing the Suitability of Mild Steel for Arc Welding.** S. G. P. de Lange and E. S. Waddington. (Welding, 1942, vol. 10, June, pp. 111-112). The authors describe a procedure for testing whether mild steel is suitable for electric welding. The factors to be examined fall into three groups relating to the skill of the welder and the technique employed, the electrode and the base metal. The welder is tested by giving him a joint to weld which is similar in nature to the repetition work required, and examining and testing the work done. On commencing a contract for repetition work it is recommended that one or two sample welds are first carried out, and that these welds, together with a small supply of the materials used, be kept until the completion of the contract. If difficulties are experienced later and the electrodes are suspected, they are immediately tried out on this material to see if they will give the same results as at the beginning of the contract; if difficulties are experienced it can be assumed that the trouble is due to electrodes. If, however, the electrodes are satisfactory with the original material but not with that used later on in the contract, it may be assumed that the cause of the trouble lies in the base material. A simple form of weldability test in which a T-bar is constructed with fillet welds, quenched in water and examined for cracks, is also described.

**The Shotweld Process of Welding Stainless Steel "18-8."** J. Winlock and J. J. MacKinney. (Welding Journal, 1942, vol. 21, Mar., pp. 153-157). The authors first study the properties of 18/8 stainless steel, in particular the effect of rapid heating and cooling on its strength, ductility and corrosion resistance. They then describe in detail the "Shotweld" method of resistance spot welding stainless-steel sheets, dealing in turn with the control of the following variables: (1) The material, shape and size of the electrodes; (2) the mechanical pressure applied to the electrodes; (3) the time of current flow, and (4) the amount of current. Finally, a method of constructing curves which correlate some of these variable factors is described.

**Welding the Stainless Steels.** H. S. Marquand. (Welding, 1942, vol. 10, Apr., pp. 57-59; May, pp. 79-81). The author de-

scribes the equipment and technique for electric welding stainless steel and for welding stainless steel to mild carbon steel. The tensile properties of the parent metal and the weld metal for joints in steels containing 12.5%, 15.7% and 17.5% of chromium are given, and procedures are described for the electrical resistance spot welding, oxy-acetylene welding and atomic hydrogen arc welding of stainless steel.

**Cutting Tools Tipped with High Speed Steel.** (Iron Age, 1942, vol. 149, Mar. 26, pp. 53-55). Reference is made to brazing and to arc-welding methods of fixing high-speed steel tips on to carbon or low-alloy steel shanks without affecting the hardness of the tip, so that the composite tool does not require further heat treatment. No other details of the methods are given, but several examples of composite tools made from worn down high-speed steel are described and illustrated.

**High-Speed Steel Tips Cemented to Low Alloy Shanks.** G. Shuler. (Iron Age, 1942, vol. 149, Apr. 16, pp. 35-38). The author describes a method of cementing high-speed steel tips to carbon or low-alloy steel shanks. A proprietary cement called "Cinch" is used; the surfaces to be joined must first be ground flat and coated with copper-sulphate solution. Whilst still wet the cement is applied and the two pieces are pressed firmly in position with the fingers. After setting for about an hour the tool is preheated to 1500-1550° F., and then brought up to the heat-treatment temperature specified for the high-speed steel. The excess cement is squeezed out and the tool is cooled in air or oil. Finally it is given the appropriate tempering treatment.

## MACHINING

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(Continued from p. 22 A)

**Economy in Tungsten Steels.** (Machinery, 1942, vol. 60, May 14, pp. 431-434). Some information is given on the way in which economies in the use of tungsten steel are effected at a Coventry works producing screwing dies, milling cutters and lathe and other tools. In conclusion the replacement of tungsten steel by molybdenum steel is briefly discussed.

**Materials, Cutting Tools and Machinability Index.** G. Schlesinger. (Journal of the Institution of Production Engineers, 1942, vol. 21, Feb., pp. 63-102). The author gives information on British, American and Continental steels used in automobile manufacture and presents curves and statistics relating to optimum cutting speeds, tool angles with proposed British and American nomenclature of these angles, tool angles for proprietary tool steels, British and American tool shank sizes, dynamometer tests with small and large tool dynamometers, machining tests with hard cemented-carbide



tipped tools carried out in the workshops of the London, Midland and Scottish Railway Co., and to the design and power requirements of different types of milling cutters.

**Abrasive-Disk Cutting.** A. F. Macconochie. (Steel, 1942, vol. 110, Mar. 9, pp. 88-91). The author describes and illustrates a machine for cutting metal bars by means of an abrasive disc 18 in. in dia. with an 8-in. face revolving at high speed. Very hard steels which it would be almost impossible to cut with a saw can be cut with this machine.

## CLEANING AND PICKLING OF METALS

(Continued from pp. 22 A-24 A)

**Electrolytic Cleaning of Metals.** H. R. Hanley. (Metal Progress, 1942, vol. 41, Feb., pp. 179-183). The author reviews electrolytic processes for cleaning carbon steels and stainless steels.

**"Flame-Priming" for the Protection of Steel.** (Mechanical World, 1942, vol. 111, May 22, pp. 453-454). The equipment and technique for the flame-descaling with an oxy-acetylene multi-tip burner of the inside surface of a 10-ft.-dia. water main 550 ft. long are described.

**War Products Consultation.** (Metal Progress, 1942, vol. 41, Mar., pp. 350-351). Various suggestions are made regarding the pickling of alloy steel rods and forgings, especially of 3.5% nickel steel and 1.3% chromium steel.

**Pickling Capacity Increased.** (Steel, 1942, vol. 110, Apr. 13, pp. 108-110). An illustrated description is given of the conveyor and crane system installed at the pickling plant of the Buffalo Bolt Co., North Tonawanda, which has enabled the pickling tanks to be used at full capacity. The crane has a special hook on which it can lift ten 7-cwt. coils of steel rod at a time and place them between uprights on a massive 56-ft. electrically-driven link conveyor.

**Recovery of Chemicals from Pickling Liquor and Copperas Waste.** H. W. Gehm. (Industrial and Engineering Chemistry, Industrial Edition, 1942, vol. 34, Mar., pp. 382-384). The author suggests two methods for the utilisation of pickling liquor and other ferrous sulphate waste solutions, especially those obtained on leaching ores with sulphuric acid. In the first method the waste solutions are treated with sodium silicate and soda ash. The precipitate produced is free from sulphur, so that the iron can be recovered from it. The filtrate can be used for the production of sodium sulphate. In the second method the free sulphuric acid is neutralised with scrap iron and calcium chloride is added to the solution, so that the ferrous sulphate is converted to ferrous chloride, which is readily oxidised to ferric chloride by chlorination. The calcium sulphate formed can be used as building material.

## COATING OF METALS

(Continued from pp. 24 A-25 A)

**The Electrodeposition of Metals.** S. Murray. (Journal of the Institution of Production Engineers, 1942, vol. 21, May, pp. 192-203). The author explains the theory of the electrodeposition of metals, the mechanism of a plating bath and the preparation of articles for plating, and gives brief descriptions of the methods of plating with rhodium, gold, silver, zinc, cadmium, tin, copper, nickel and chromium.

**Stainless Clad Steels.** S. L. Hoyt. (Metal Progress, 1942, vol. 41, Jan., pp. 51-53). The author briefly describes five methods by which stainless clad steel is made, and suggests that much greater use of this steel should be made to replace solid stainless steel, thus saving considerable amounts of chromium and nickel.

**New Cladding Method.** (Steel, 1942, vol. 110, Mar. 30, p. 62). A brief description is given of the Jessop method of manufacturing stainless-clad steel sheet. Two slabs of stainless steel with a separating compound between them (composition of compound not stated) are inserted between two mild steel slabs. Steel bars are tack-welded along the edges of the stainless steel and the latter is sealed within the mild steel slabs by machine welding all round the edges. This composite block is then rolled out under great pressure, which welds each stainless steel sheet to its mild steel backing. The welded edges are afterwards cut away and the pair of clad sheets is separated.

**Manufacture of Alloy-Clad Steel.** (Steel, 1942, vol. 110, Apr. 20, p. 82). Several photographs, with explanatory text, are reproduced which show the first application in the United States of a process in extensive use in Europe for the production of copper- and copper-nickel-clad steel.

**Cadmium Plating in the Victory Program.** A. J. Fusco and N. E. Woldman. (Iron Age, 1942, vol. 149, Mar. 19, pp. 46-52). Some properties of cadmium coatings and characteristics of the plating process with special reference to speed of deposition and ease of control are pointed out and a fairly detailed description of the process as carried out at an American aircraft factory is given.

**Helpful Notes and Data on some Metal Colouring Processes.** (Sheet Metal Industries, 1941, vol. 15, Dec., pp. 1513-1515; 1942, vol. 16, Jan., pp. 47-49; Feb., pp. 181, 182, 188; Mar., pp. 319-321). The author discusses various processes of metal colouring, which is generally understood to mean colouring by chemical means, with or without the aid of an electric current, as opposed to painting or enamelling. The methods of preparation include: (a) cleaning and removing scale, (b) polishing or etching, and, if necessary, (c) the electro-deposition of a metal more suitable for colouring than the base metal. These methods are described in Part I., and the

colouring of aluminium and its alloys is described in Part II. Part III. is devoted to methods of colouring iron and steel. The blackening of steel in a bath containing a mixture of sodium hydroxide and sodium nitrate held at  $145^{\circ}\text{C}$ . is first described, and details are then given of solutions in which a chloride, usually antimony chloride, is mixed to a paste with olive oil or similar organic substance and then applied to the surface, which should be preheated to about  $150^{\circ}\text{C}$ . The phosphate processes are also considered, although these are used more for corrosion resistance than for colouring. The treatment of copper and its alloys is dealt with in Part IV., and details of solutions for the electrolytic deposition of (a) black nickel coatings; (b) tin coatings on brass, copper and copper-plated iron; (c) tin direct on steel; and (d) copper and brass on iron and steel, are given in Part V.

**Phosphate Coatings on Steel.** H. Chase. (Metals and Alloys, 1942, vol. 15, Mar., pp. 420-424). Illustrations of parkerising and bonderising plants for depositing phosphate coatings on steel are presented and the advantages of these coatings are discussed. Reference is also made to Parco-Lubrite treatment, which is similar to parkerising, and is applied to automobile engine parts such as camshafts, valve tappets, piston rings and rocker arms; this treatment reduces wear during running-in periods and the coating absorbs and retains lubricant.

**Anodic and Surface Conversion Coatings on Metals.** J. D. Edwards. (Electrochemical Society, Apr. 1942, Preprint No. 81-18). The author reports on the production and properties of oxide coatings, dealing especially with aluminium, magnesium and zinc. In the concluding paragraph he briefly reviews the most important processes for the production of oxide coatings on iron and steel.

**Heat Requirements for Hot Dip Galvanizing.** W. G. Imhoff. (Steel, 1942, vol. 110, Apr. 27, pp. 80-86). The author presents and discusses data relative to the heat requirements for hot-dip galvanizing. The proportion of the total wall area of a galvanising bath to which heat is actually applied is usually about 60%. Data from plant in the United States on the heat input per square foot of bath area in relation the bath life indicate that satisfactory results are obtained with 8000-10,000 B.Th.U. per hr. per sq. ft. passing through the sides of the bath. For starting up a large galvanising pot, about 300,000 B.Th.U. per ton of zinc are required, and for heating up the material to be galvanised about 160 B.Th.U. per lb. are needed. Covering a bath during idle time reduces the heat loss by about 60%.

**Practical Problems in Electrotinning.** S. Baier. (Journal of the Electrodepositors' Technical Society, 1942, vol. 17, pp. 105-127). The author deals with the problem of carrying out electrotinning in the most efficient way, especially with regard to the economic use of the supplies available in war-time. After an introduction, in which the importance is emphasised of the selection of a suitable thickness of coating and of its uniformity, he deals separately with basic stannate

and acid sulphate baths, discussing especially the composition and control of the bath solutions, the working temperature and time, the types and numbers of anodes to be used, and the anodic and cathodic current density.

**New Work on Timplating from Ammonium Stannous Oxalate.** F. C. Mathers and P. H. Johnson. (Electrochemical Society, 1942, Apr., Preprint No. 81-7). The authors studied the effect of various additions to ammonium stannous oxalate baths, and found that "hydrolysed glue" has the same favourable effect as peptone, which was recommended previously, and the former has the advantages of being cheaper and less liable to bacterial decomposition. They prepare the hydrolysed glue by boiling 10 g. of animal glue for 10 hr. in 100 c.c. of water, and recommend the addition of 1 g. of the product obtained to 1 litre of the electrolysis solution, containing 60 g. of ammonium oxalate, 50 g. of stannous oxalate, 15 g. of oxalic acid, 15 g. of potassium iodide and 1 g. of pyrogallol. They investigated the causes of the gradual deterioration of tin oxalate baths during use, and found that this was due to the oxidation of stannous to stannic ion, and that the bath could be regenerated by boiling for  $1\frac{1}{2}$  hr. with spongy tin. There is less oxidation of the bath if spongy tin or tin foil are used for the anodes instead of cast tin.

**Automatic Metal Spraying.** (Steel, 1942, vol. 110, Mar. 9, pp. 92-94). An illustrated description is given of a metal-spraying machine for the automatic spraying with molten aluminium of aero-engine cylinders. These cylinders for air-cooled engines have very deep recesses between the fins, and the spraying machine is designed with six bays and six spraying pistols, which travel up and down the cylinders while the latter are rotated.

**Cause of Defects in Enamel Fired on Cast Iron at Temperatures above 725° C.** C. A. Zapffe. (Journal of the American Ceramic Society, 1942, vol. 25, Apr., pp. 175-180). The author reports on an investigation of the defects in enamel coatings on cast iron fired at temperatures of 730°, 790°, 840° and 870° C. His conclusions were: (1) Hydrogen is apparently the only cause of the blister type of defect in wet-process enamel coatings on cast iron fired at up to 870° C. When the oxides of carbon were formed during the enamelling, they did not occur in sufficient quantities to deface the surfaces of the specimens used in the tests. (2) No blisters developed in enamels fired at 790° C. on cast iron from which the hydrogen had been removed. (3) When firing enamelled cast iron, hydrogen does not pass into the iron as it does into steel; any hydrogen released from the hydrate in the coating combines with the carbon in the iron to form methane, and this gas escapes, and thus causes some decarburisation of the iron. (4) Cast iron is less susceptible than steel to fish-scaling.

**Scratch Blisters.** C. A. Zapffe and J. L. Yarne. (Journal of the American Ceramic Society, 1942, vol. 25, Apr., pp. 180-190).



The authors report on an investigation of the causes of the blisters which occur in enamel coatings on steel sheets above scratches in the steel; they are known as "scratch blisters." This blistering is consistently caused by the liberation of hydrogen, but the mechanism is not simple, because the excess of hydrogen may come from more than one source. Scratch blisters occur when steel, with a certain type of tenacious oxide coating, is scratched before pickling, because the electrochemical and physical effects of the scale increase the hydrogen absorption at the scratch. Blisters may also form over scratches in nickel-plated steel, because at the scratch the moisture in the enamel is free to react with the iron.

**Relation of Surface Oxidation to Certain Defects in Enamel Coatings on Steel.** C. A. Zapffe and J. L. Yarne. (Journal of the American Ceramic Society, 1942, vol. 25, Apr., pp. 191-194). The authors studied the influence of oxide coatings on steel on the occurrence of defects in subsequent enamel coatings. The oxide on the surface of steel sheet plays an important part in controlling defects in subsequent enamelled coatings. If the surface of the steel is pre-oxidised to obtain a uniform coating of certain characteristics, the amount of hydrogen evolved during firing is reduced so much that a white enamel cover coat can be fired directly on the steel without danger of blisters, reboiling and fish-scaling. If the steel is held for a few minutes at 760° C. in an electric furnace an oxide coating will be produced which will have the above desirable effect.

**Chips, Fish Scales and Shiners.** C. A. Zapffe and J. L. Yarne. (Journal of the American Ceramic Society, 1942, vol. 25, Apr., pp. 194-203). The authors report on research to examine more closely the extent of the defacement of enamel coatings which occurs when hydrogen attempts to escape after the enamel has solidified. The defacement ranges from chips (a form of flaking which exposes the metal), through fish scales, down to "shiners" (small light-coloured markings). The difference in the appearance of these defects was found to depend principally on differences in: (1) The physical properties of the enamel; (2) the metal-enamel bond; and (3) the rate, quantity and locality of the hydrogen evolution.

**Further Considerations of Hydrogen as a Cause of Enamel Defects.** C. A. Zapffe and C. E. Sims. (Journal of the American Ceramic Society, 1942, vol. 25, Apr., pp. 205-215). The authors discuss factors affecting the absorption and evolution of hydrogen from steel and their influence on the occurrence of defects in enamel coatings. The impurities that collect in pickling acid may greatly increase the occurrence of defects of the blister type. Inhibitors in pickling solutions decrease the evolution of hydrogen, but they may have unexpected effects on the amount of hydrogen absorbed. A smooth galvanic nickel coating reduces the boiling of enamel on firing, but a nickel coating broken by scratches or roughness of the steel causes boiling, which appears to be more severe than that developed on firing enamel on bare iron. Hydrogen in steel at

ordinary temperatures is occluded within ultramicroscopic rifts which constitute a network throughout the interior of each grain, and heating the steel causes the cyclic evolution and reabsorption of the hydrogen into these rifts. It is suggested that the preliminary increase in temperature expands the gas in these rifts and raises the pressure so as to expel a portion of the gas, but the evolution soon stops and reabsorption takes place because of the increase in the hydrogen-solubility with rising temperature.

**Paint Coatings Substituted for Metallic Zinc Coatings.** E. F. Hickson. (Steel, 1942, vol. 110, Jan. 12, pp. 74-78). The author makes recommendations on the types of paint most suitable for painting steel to replace galvanised steel for in-door and out-door use under different conditions. The paints are classified in accordance with various American specifications, brief particulars of which are given.

## PROPERTIES AND TESTS

(Continued from pp. 67 A-74 A)

**Cast-Iron.** (Automobile Engineer, 1942, vol. 30, June, pp. 237-242). The possibility that more cast iron may be used in the post-war motor-car is discussed at considerable length. After referring to units that do not lend themselves to construction in cast iron, a list of parts is given for which this material is especially suitable. Cylinder blocks are considered first, and a survey is made of recent investigations into bore wear. Cylinder liners are dealt with next, then piston rings and other units, some of which are only in the experimental stage. In conclusion, the various alloys of cast iron are described and their advantages enumerated.

**Getting Maximum Results from Carbon and Low Alloy Steels.** H. W. McQuaid. (Nassau, 1942, vol. 4, Jan., pp. 3-10; Feb., pp. 4-15; Mar., pp. 5-11). The author discusses how different additions and different forms of heat treatment affect the properties of carbon steel and low-alloy steels. On simple shapes, and with special equipment, "timed" water or caustic quenching of an ordinary carbon steel will produce a satisfactory structure, but the subsequent tempering temperature will have to be so low that there will be high residual stresses; to raise this tempering temperature the steel should contain about 1% of manganese, with smaller amounts of such elements as chromium, molybdenum or nickel. For steel of larger dimensions more of the alloying element is required. In parts where stress is maximum at the surface, a carbon content close to the eutectoid composition will result in surface structures having the best combination of strength and ductility at high hardness. Data are presented on the timed quenching of Ford axle shafts of 0.40% carbon steel.

The water-quenching of alloy steels is uncommon, and it is not recommended except in special circumstances, such as for large alloy steel shafts, especially if the carbon content is low. An example of the high hardness and strength developed in a 0.40% carbon steel to which 1 lb. of dehydrated borax per ton was added is quoted; specimens 0.530 in. in dia. turned after normalising, then quenched in oil from 1550° F. and tempered at 450° F., developed a tensile strength of 127 tons per sq. in., 11% elongation on 2 in., 43% reduction of area and a hardness of Rockwell C 50. The addition of borax is most effective in the carbon range 0.20–0.45%, which may be due to the fact that in this range any boundary ferrite remaining in the quenched and tempered structure is most effective in reducing ductility. Wherever the microstructure combines martensite or tempered martensitic grains with ferrite boundaries it is found that, when the specimen is subjected to tensile stress, the stress will tend to be thrown by the stiff unyielding grains into the softer ferrite boundaries and there concentrated. It is commonly assumed that the mixture of martensite and ferrite obtained on quenching hypoeutectoid steels from *within* the critical range on heating will result in poor ductility, but it is not so well known that a similar type of structure, obtained by relatively slow cooling during quenching *through* the range of temperature where the austenite and ferrite are both stable, is also conducive to lowered ductility. The maximum effect of ferrite in the boundaries of a quenched steel on the ductility occurs when it is in combination with fully hardened martensitic grains. Quenching studies show that both vanadium and chromium tend to increase rather than decrease the amount of ferrite in a structure obtained at about 1000° F. with oil-quenching, as compared with manganese, nickel and molybdenum; it follows that, when oil-quenched, manganese, nickel and molybdenum steels at high hardness should give better combinations of ductility and strength than the chromium or vanadium types. With regard to case-hardening steels, there is no doubt that higher-carbon steels can be used for carburising, providing they are fine-grained. Where some ductility of the case is of considerable importance the carburising procedure, if possible, should be such that a eutectoid composition is obtained in the case. To develop the best properties in carburising steels, it is necessary that the carbon content be such that when oil-quenched the core strength will be satisfactory. Since the ductility of the core is usually of minor importance, the strength of core to suit a given case depth can be obtained most easily by increasing the carbon content. Several S-curves for low-alloy steels as well as data from Jominy end-quench tests are presented, and are applied to develop and illustrate the author's statements. (*See also* Journ. I. and S.I., 1942, No. I., p. 147 A).

**Properties of Heavy Forgings.** G. Sachs. (Steel, 1942, vol. 110, Apr. 6, pp. 76–77, 101–109). The author reviews the literature on the properties of steel forgings.

**Exact Definitions of the Words "Bruch" and "Riss."** R. Walzel. (Stahl und Eisen, 1942, vol. 62, May 28, pp. 456-458). The author urges the correct application of the German words *Bruch* and *Riss* which are in most cases translated as fracture or breakage, and crack or flaw, respectively, and he makes various suggestions regarding the terminology of special cases of fracturing and cracking.

**Tensile Elastic Properties of Nickel, Copper, Open-Hearth Iron, and Typical Steels.** D. J. McAdam, jun., and R. W. Mebs. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Mar., pp. 311-378). The authors report on their investigation of the elastic properties of nickel, oxygen-free copper, open-hearth iron and three steels containing respectively 0.20%, 0.42% and 0.73% of carbon. The apparatus used is described. From the data obtained stress-strain and stress-set curves were drawn, the stresses required to cause permanent extensions of 0.001%, 0.003%, 0.01%, 0.03% and 0.1% were noted and the moduli of elasticity were calculated. With prior plastic extension, the proof stresses representing permanent set values of 0.03% and 0.1% generally increase continuously. The 0.001% proof stress, and sometimes the 0.003% proof stress, do not increase or decrease continuously, but either increase to a maximum or decrease to a minimum; beyond these points these proof stresses fluctuate with little or no general upward trend. The variation of the proof stresses with prior plastic extension is affected by the rate of work-hardening, by the change of internal stress and by the duration of the rest period between the determinations of the plastic extension and the stress-set data. The curves for the variation of the elastic moduli with plastic extension are affected by variation of crystal orientation, internal stress, lattice expansion and by rest. The curves for the variation of the stress coefficients of the elastic moduli are affected by all these factors except perhaps the reorientation factor.

**The Technical Cohesive Strength of Metals.** D. J. McAdam, jun. (Journal of Applied Mechanics, 1941, vol. 8, Dec., pp. A-155-A-165). In surveying the literature the author has found evidence incompatible with prevalent views regarding the technical cohesive strength of metals. In this paper some of the evidence is assembled for discussion, with special reference to the criteria of fracture and the variation of the technical cohesive strength with plastic deformation.

**The Steelmakers' Viewpoint.** D. Taylor. (Automobile Engineer, 1942, vol. 32, June, pp. 230-234). The author discusses complaints made by the users of steel to the manufacturers, and cites several examples from actual experience of complaints relating to defects revealed by machining, forging, drawing and heat-treatment operations for which the steelmakers was blamed, but which, on more thorough investigation, were found to be due to selection of unsuitable material, insufficient machining allowances, poor design or faulty heat treatment.



**Scatter in Hardness Tests on Steel.** W. Hengemühle. (Stahl und Eisen, 1942, vol. 62, Apr. 16, pp. 321-328). The author discusses the errors which, even with most careful experimental technique, are inevitable in Brinell, Vickers and Rockwell hardness tests, owing to inherent irregularities in the shapes of the indentors, and to unavoidable errors in the loading and reading of the testing machines. He reports on experiments in which he determined the magnitude of these errors, so that he could calculate the minimum scatter to be expected in the results. With the aid of some practical examples he describes his new method for the mutual conversion of Brinell, Vickers and Rockwell hardness values taking the inherent errors of the tests into account, and presents conversion curves and tables obtained by his method; these show the corresponding mean values obtained by the three test methods as well as the deviations from the mean values which are to be expected in each method.

**How to Identify Alloy Steel Scrap.** L. P. Tarasov. (Iron Age, 1942, vol. 149, Apr. 16, pp. 39-43). The author describes the classification of steel by spark testing and points out the limitations of the technique. When nothing is known about the composition and origin of the pieces to be sorted, it can be roughly classified by sparking into the plain carbon and low-alloy group, the stainless group, and the tool and die group. A portable grinder, a pair of safety goggles and a set of standard samples of known composition comprise the equipment required.

**Magnetization near Boundaries.** J. H. Wakelin, jun. (Journal of Applied Physics, 1942, vol. 13, Apr., pp. 227-235). The author describes experiments carried out to discover whether small differences in the distribution of magnetism in a material with change of its specific surface could be discovered by ballistic measurements. Ring samples of silicon iron, commercially pure nickel and low-carbon steel 6-350 cm. outside dia. and 5-042 cm. inside dia. in the thickness range  $3.8 \times 10^{-3}$  to  $38.1 \times 10^{-3}$  cm. were used, and the magnetic measurements indicated that it is possible to detect surface stray flux contributions to the total magnetism by comparing the hysteresis loops obtained at a maximum applied field of 4 oersteds. The magnetic quality appears to be insensitive to changes of specific surface, but the evidence suggests the presence of a surface layer of low permeability.

**Effect of Cold-Rolling and Annealing on the Watt Loss of Dynamo and Transformer Strip Steel.** A. Pomp and H. Wübbenhorst. (Stahl und Eisen, 1942, vol. 62, June 4, pp. 482-487). The authors studied the effect of the degree of cold-deformation and of the annealing temperature and time on the watt loss of three basic open-hearth steels containing respectively 0.75%, 2.03%, and 4.05% of silicon. They found that with relatively low annealing temperatures even small reductions lead to favourable watt-loss values. With high annealing temperatures (above 1000° C.) the degree of cold-deformation does not affect the watt loss at all. The authors

recommend, however, annealing low-silicon dynamo and transformer steel at temperatures below  $900^{\circ}\text{C}$ ., so that the upper transformation point cannot be exceeded. High-silicon steels should be annealed at temperatures above  $1000^{\circ}\text{C}$ ., although such high temperatures lower the bending strength. The watt loss of specimens of the two higher-silicon steels annealed in continuous furnaces were equal and sometimes even smaller than those of box-annealed specimens. For the 0.75% silicon steel, however, the short annealing period in the continuous furnace did not lead to satisfactory watt-loss values.

**The Effect of Nitrogen in Austenitic and Austenitic-Ferritic Chromium-Nickel Steels.** R. Scherer, G. Riedrich and H. Kessner. (Stahl und Eisen, 1942, vol. 62, Apr. 23, pp. 347-352). After a brief review of the literature on the effect of nitrogen in chromium and chromium-nickel steels, the authors report on their study of the effect of nitrogen on the strength properties, the structure and the heat and corrosion resistance of chromium-nickel steels containing between 6% and 25% of chromium and between 1% and 13% of nickel. The investigation led to the following conclusions: (1) The 0.2% proof stress of austenitic chromium-nickel steels, and of austenitic-ferritic chromium-nickel steels with over 30% of austenite, is increased by about 8 kg. per sq. mm. by the presence of 0.10-0.12% of nitrogen. (2) The other strength properties are not noticeably affected, provided that the structure has remained unaltered. (3) With regard to the structure, 0.15% of nitrogen can replace about 2-4% of nickel, and 0.25% can replace about 2.5-6% of nickel, depending on the chromium content, because nitrogen has the effect of increasing the stability of the austenite phase of chromium-nickel steels. This is of special practical importance in 18/8 chromium-nickel steels. (4) The susceptibility to embrittlement on annealing at higher temperatures is not affected by nitrogen. (5) Austenitic and austenitic-ferritic steels with about 0.10% of carbon, 21-25% of chromium, 4-5.5% of nickel and about 0.20% of nitrogen are recommended as oxidation- and acid-resistant material, and an austenitic steel with about 0.15% of carbon, 22% of chromium, 13% of nickel, 1.5% of silicon and 0.20% of nitrogen is suggested as a substitute for certain heat-resistant steels containing about 0.15% of carbon, 25% of chromium, 20% of nickel and 2% of silicon.

**Boron—A New Vitamin for Steel and Cast Iron.** N. F. Tisdale. (Metal Progress, 1942, vol. 41, Mar., pp. 330-331). The author briefly discusses the effects of additions of boron to steel and cast iron, pointing out that steels containing more than 0.003% of boron are often liable to hot-shortness, whereas as much as 0.02-0.10% is added with beneficial results to cast irons.

**The Effect of Thorium on Cast Iron.** W. Baukloh and H. Meierling. (Giesserei, 1942, vol. 29, Mar. 20, pp. 93-94). The authors report on an investigation of the effects of additions of from 0.2% to 1.0% of thorium on the properties of grey cast iron. Thor-

ium reduced the viscosity of molten cast iron and improved the bend and tensile strengths, chiefly because of its action in increasing the fineness of the graphite. It also had a desulphurising effect.

**The Effect of Phosphorus on the Strength Properties of Cast Steel from a Small Bessemer Converter.** H. Heinrich. (Giesserei, 1942, vol. 29, Apr. 3, pp. 115–117). The author describes an investigation of the properties of cast steel containing carbon 0.12%, silicon 0.23%, manganese 0.50%, phosphorus 0.068% and sulphur 0.017% made in a small Bessemer converter, in order to discover whether the phosphorus is responsible for the brittleness sometimes observed with this steel. It was found that phosphorus could cause precipitation hardness and poor impact properties even in well-deoxidised Bessemer steel. The following heat treatment is recommended for castings of wall-thickness up to 65 mm.: annealing at about 50° C. above the G-O-S line and cooling at a velocity greater than 40° C. per hr.

**The Degree of Saturation of Cast Iron.** F. Bischof. (Giesserei, 1942, vol. 29, May 1, pp. 153–156). The author reviews the literature on the effect of silicon on the degree of carbon saturation in cast iron as expressed by the formulæ developed by Heyn and Piowarsky.

**Possible Alternates for Nickel, Chromium and Chromium-Nickel Constructional Alloy Steels.** (American Iron and Steel Institute: Contributions to the Metallurgy of Steel, No. 5, 1942). This is a report, prepared at the request of the Office of Production Management (U.S.A.), by a committee selected by the American Iron and Steel Institute and the Society of Automotive Engineers. It consists mainly of data on the properties of unalloyed, and of low-alloy nickel, chromium and nickel-chromium steels which are proposed as alternatives to the higher alloy constructional steels the use of which is now prohibited for many purposes.

**Tungsten Economy in High-Speed Tool Steels.** (Engineer, 1942, vol. 173, May 29, pp. 452–453). Some properties and limitations of the molybdenum high-speed steels which are now being used as a result of the order that no more tools containing more than 6.5% of tungsten are to be manufactured are discussed and the advantages of tools tipped with tungsten carbide are pointed out.

**The Material for Cylinders for Internal Combustion Engines.** C. W. Pfannenschmidt. (Giesserei, 1942, vol. 29, Mar. 6, pp. 74–78). The author reviews the literature on the development of cast iron suitable for making Diesel engine cylinder liners.

**Soft Steels for Plastic Molds.** H. C. Disston and J. K. Desmond. (Metal Progress, 1942, vol. 41, Apr., pp. 512–514). The authors advocate the use of soft steel or low-carbon iron instead of low-alloy steels for making moulds for pressing plastics. They discuss the cleanliness, machinability, hardenability, possibility of distortion in heat treatment and the service life of heat-treated soft steel. The usual working pressure on these moulds is 1–2 tons per sq. in., and

as the elastic limit of the soft steel is 20–22 tons per sq. in. there is no possibility of any permanent set. The authors recommend carburising the soft steel at 1750° F. with a direct quench into oil and a subsequent grain-refining treatment. This material is much more easily hobbled than low-alloy nickel-chromium steel and, with proper heat treatment, a very satisfactory life is obtained for dies made of it.

**The Present Stage of Development of Heat-Resistant Cast Steel.** F. Schulte. (Stahl und Eisen, 1942, vol. 62, May 7, pp. 389–397). The author gives a detailed review of the more common compositions, the mechanical and scaling-resisting properties, the casting properties and the uses of chromium-molybdenum cast steels of high hot-strength and of heat-resistant chromium cast steels—including *Chromguss*, i.e., steels with 20–30% of chromium and 1–1.5% of carbon, the casting and strength properties of which greatly resemble those of high-class cast iron—as well as those of heat-resistant chromium-nickel and chromium-manganese cast steels. Special consideration is given to the possibility of replacing molybdenum in hot-strength castings, and chromium and nickel in heat-resistant castings.

**Heat-Resisting Steels.** G. Riedrich. (Engineer, 1942, vol. 173, June 12, pp. 499–501). An abridged English translation is presented of the author's paper on the properties of rolled and forged heat-resisting steels which appeared in Stahl und Eisen, 1941, vol. 61, Sept. 11, pp. 852–858. See Journ. I. and S.I., 1942, No. I., p. 245 A.

**Correlated SAE and AISI Revised Standard Steels.** (Iron Age, 1942, vol. 149, Apr. 9, pp. 66–68). Lists of analyses of carbon steels, free-cutting steels and alloys which were published as revisions to the "Combined Standard Steel Lists of the American Iron and Steel Institute and the Society of Automotive Engineers" are presented; the specification numbers of these two bodies are also shown.

**Specifications for Steel.** D. M. Mills. (Australian Institute of Metals: Australasian Engineer, 1942, vol. 42, Mar. 7, pp. 9–10, 33–42). The author details and discusses the efforts being made to reduce and co-ordinate the numerous specifications which exist in the English-speaking countries. He considers in turn the steel position in Australia according to the requirements of industry in general, the Navy, the Army, the Air Force and the export trade. In two appendices he gives a specimen standard specification for steel plates and a list of Australian standards for iron and steel.



## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 74 A-78 A)

**The Training of the Young Metallurgist.** D. G. P. Paterson. (Sheet Metal Industries, 1942, vol. 16, Feb., pp. 183-185, 188; Mar., pp. 322-324; Apr., pp. 462-465; May, pp. 601-603). The author describes some of the fundamental scientific and practical studies which are necessary in the training of young metallurgists. In the first part of the paper the principles of thermo-electric and optical pyrometers, cooling curves, equilibrium diagrams, the principles of the microscope, oxidation and reduction, and annealing problems are simply and briefly explained. In the second part the fundamentals of the production of metals from ores are dealt with and the value of data obtained by tensile, hardness, impact, fatigue, bend and cupping tests is explained.

**The Production of High-Class Micrographs of Cast Iron and Malleable Cast Iron.** M. Krichel. (Giesserei, 1942, vol. 29, Mar. 6, pp. 78-82). The author makes recommendations with regard to polishing procedures for preparing metallographic specimens of cast iron and presents micrographs of specimens of iron with coarse graphite, an iron melted under vacuum having very fine graphite particles and a ferritic cast iron with normal graphite. These illustrations show the effects of too little and too much polishing.

**Microscopic Examination of Metals.** J. B. Bassett. (American Society for Metals: Canadian Metals and Metallurgical Industries, 1942, vol. 5, Mar., pp. 72-77). The author describes the cutting and etching of specimens for metallographic investigation and the principles of the microscope, giving some examples of the microstructure of steel and their interpretation.

**Standardised Methods for Determining Austenitic Grain Size of Steel.** (Metal Progress, 1942, vol. 41, Mar., pp. 332-334). Exact experimental details are given of the standard procedures developed by the Steel Standardisation Group (a committee of representatives of leading American steelworks) for the McQuaid-Ehn as well as the oxidation method of determining the austenitic grain size of steel.

## CORROSION OF IRON AND STEEL

(Continued from pp. 78 A-80 A)

**Cathodic Protection.** R. H. Brown. (Electrochemical Society, Apr. 1942, Preprint No. 81-19). The author gives an extensive review of literature of interest in connection with cathodic protection against corrosion and reports on his own theoretical and experimental study of this subject, which led to the following conclusions :

(1) For the achievement of complete protection the potential of the cathode areas must be polarised to a potential equal to or more anodic than the "open-circuit" potential of the anodes, depending on whether the cathodic polarisation is large or small compared with the drop in resistance. (2) The current required for complete protection depends (a) on that required for the polarisation of the cathode, (b) on the position of the auxiliary anode relative to the positions of the local anodes and cathodes, and (c) on the drop in potential between the auxiliary anode and the local cathodes. (3) The products of electrolysis resulting from the application of cathodic current may cause special attack or inhibition. Certain types of attack on surfaces made cathodic may be beneficial however.

**Corrosion of Binary Alloys.** R. Landau and S. Oldach. (Electrochemical Society, Apr. 1942, Preprint No. 81-16). The authors carried out a systematic study of the effect of the proportions of the alloy components of iron-cobalt, iron-nickel, iron-manganese and four non-ferrous binary solid-solution alloys on the electric potentials and the corrosion in sodium chloride, ammonium chloride, hydrochloric acid, nitric acid and sulphuric acid, in the absence and presence of air. They discuss their results and data published in the literature on the above and other alloy systems, laying special stress on the difference between the passivating influence of metals like chromium, molybdenum and tungsten, and the lesser improvement in corrosion resistance resulting from the dilution with noble metals, *e.g.*, palladium.

**Some Mechanisms of Alloy Corrosion.** R. Landau. (Electrochemical Society, Apr. 1942, Preprint No. 81-23). The author discusses the experimental data presented previously by himself and S. Oldach (*see* preceding abstract) with a view to clarifying the mechanism of the corrosion of alloys. By extending the local cell theory so as to cover alloys, he succeeds in explaining the general shapes of the corrosion-rate/composition curves observed for various alloy series. He shows that in passivating media these curves are largely determined by the stability of the passive film formed in the media in question, so that the curves are functions of both the alloy structure and the surrounding solution. In non-passivating media, however, the curves depend mainly on electrochemical factors, the influence of the alloy composition in producing abrupt changes in corrosion rates being not readily evident; and passivity limits observed here in the curves are probably largely due to factors external to the metal, *i.e.*, the relationships of anode and cathode potentials. In conclusion the author points out that although there appear to be certain phenomena, such as minima in the corrosion curves and stability of passivating films, which are probably related to the electronic structure of the alloy, it is as yet difficult to separate these inherent effects of the metal from the general electrochemical conception of corrosion, so that various older theories of alloy corrosion have to be treated with reserve.

**Corrosion-Resistance of Nickel-Chromium Steels.** R. A. Collcott. (Journal of the Junior Institution of Engineers, 1942, vol. 52, June, pp. 121-127). The author surveys the general problem of corrosion, quoting the results of experiments published recently in the technical press. In an appendix a single potential method for the detection of initial corrosion is described; in this method a sensitive potentiometer is used to measure the potential difference between a specimen of the metal under test and a standard calomel cell.

**An Outline of the Electrolytic Corrosion of Buried Metallic Structures.** T. H. D. Page. (Transactions of the South African Institute of Electrical Engineers, 1941, vol. 32, July, pp. 230-243). The author discusses the corrosion of buried metallic structures such as cable sheaths, water- and gas-pipes and reinforcing bars in concrete. After describing and illustrating several examples of this form of corrosion, stray currents in the form of circulating currents developed in the buried system itself, or as set up by electric traction systems, are dealt with at length, with special reference to conditions in the Witwatersrand area. The author devotes considerable attention to the mitigation of the corrosion of the lead sheathing of buried cables and to measures that can be applied to traction systems in order to remove, or at least greatly reduce, the flow of stray traction currents.

**Soil-Corrosion Studies, 1939: Ferrous and Non-Ferrous Corrosion-Resistant Materials.** K. H. Logan. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Mar., pp. 379-400). The author reports the condition of specimens of a variety of ferrous metals and alloys, and copper and copper alloys exposed in various soils for seven years, as well as the results of inspections of nine alloy irons and steels and of several varieties of zinc and lead exposed for two years. Little difference was observed in the corrosion resistance of the wrought iron, low-carbon steel, copper-molybdenum open-hearth iron, and steel containing 4-6% of chromium.

**Corrosion Study of Bolting Materials and Coatings.** O. A. Halvorson. (Journal of the American Water Works Association, 1942, vol. 34, Jan., pp. 76-84). After a general and elementary discussion of corrosion the author reports the results of some tests in which twenty specimens of bolts as used for buried water-pipe fittings by the Milwaukee Water Works were buried in glass jars containing respectively clay, sand, cinders and soil. The bolts were representative of five types of material: mild steel, cadmium-plated wrought iron, Z-metal (a malleable cast iron), galvanised mild steel and wrought iron. In these tests the galvanised steel corroded the least. The greatest corrosion on each type of material occurred with the bolts buried in cinders. The corrosion varied more with the nature of the soil than with the material of the bolts. For iron the author favours coal-tar enamels as giving uniformly good and economical results in the protection of water-supply systems against corrosion.

**Electrolytic Behaviour of Ferrous and Non-Ferrous Metals in Soil-Corrosion Circuits.** I. A. Denison. (Electrochemical Society, Apr. 1942, Preprint No. 81-17). The author studied the behaviour of specimens of low-carbon steel, two varieties of stainless steel, zinc, copper, brass and lead exposed to corrosion in soils with widely different chemical and physical properties. A specially designed corrosion cell, described previously (*see* Journ. I. and S.I., 1937, No. I., p. 54 A) was used for the investigation. The current required to bring the electrodes of the corrosion cell to the same potential was selected as the measure of the corrosion of steel and zinc and, in certain cases, also of the other metals and alloys studied. The corrosion rates found in the laboratory are compared with the results of long-time field tests. Both series of tests were in agreement in so far as they indicated whether or not the materials were liable to serious corrosion in the different soils. Zinc, however, which was corroded more rapidly than steel in the laboratory, proved to be more resistant than steel in the field tests. The author attributes the relatively greater corrosion resistance of zinc in the field tests to the partial suppression of anodic areas by cathodically formed alkali.

**The Effect of Hydrochloric Acid Plus Inhibitor on the Corrosion Resistance of 18/8 Stainless Steel.** H. H. Uhling and E. M. Wallace. (Electrochemical Society, Apr. 1942, Preprint No. 81-25). In a study of the passivating effect of nitric acid on 18/8 chromium-nickel steel the authors found that treatment with 3*N* to 12.5*N* hydrochloric acid containing an inhibitor accomplishes much the same thing. The authors conclude from this finding that the passivating effect of nitric acid is not due to the formation of a protective oxide film, but to the preferential solution of anodic areas in the steel surface, so that an electrochemically homogeneous surface, free from "pit nuclei" remains. Oxidising acids and anodic treatment have an additional beneficial effect, however, in that they remove hydrogen from the surface of the steel.

**"Null" Methods Applied to Corrosion Measurements.** J. M. Pearson. (Electrochemical Society, Apr. 1942, Preprint No. 81-21). The author points out that in his paper the term "corrosion measurement" means the measurement of electrode potentials, with specific attention to corroding electrodes in aqueous solutions. He gives a detailed description, with numerous diagrams, of a complicated apparatus which he developed for his study and presents a mathematical discussion of the principles underlying its construction.

**Thin Oxide Films on Iron.** E. A. Gulbransen. (Electrochemical Society, Apr. 1942, Preprint No. 81-15). The author developed a vacuum microbalance, the construction and use of which is described at some length. With its aid he measured the oxidation of pure electrolytic iron at 25°, 100°, 200°, 300° and 400° C. and at various oxygen pressures. The results obtained are correlated with the various mechanisms proposed for oxidation reactions and the



suggestion is made that the total rate of the oxidation may be the result of three components, these being (1) a rapid initial rate; (2) an intermediate rate involving the logarithm of the difference between an extrapolated value and the experimental value as a function of time; and (3) a rate obeying a parabolic law found to be valid above a certain temperature and film thickness.

**Theory of Oxidation and Tarnishing of Metals. I. The Linear, Parabolic and Logarithmic Laws.** H. A. Miley. (Electrochemical Society, Apr. 1942, Preprint No. 81-14). After a review of the literature on the three laws governing the corrosion of metals, *i.e.*, the linear, parabolic and logarithmic laws, the author shows that an electrochemical interpretation of the ionic theory provides a common basis for developing these laws and that it is theoretically possible for a film to obey two or even all three of them in turn.

## BOOK NOTICES

(Continued from p. 84 A)

PIGOTT, E. C. *The Chemical Analysis of Ferrous Alloys and Foundry Materials. Modern Practice and Theory.* With a Foreword by N. D. Ridsdale. 8vo, pp. xv + 362. Illustrated. London, 1942: Chapman and Hall, Ltd. (Price 28s.)

This book, in some ways, is a useful contribution to the literature of ferrous metallurgical analysis.

It is divided roughly into three Sections. Section I., of about 20 pages, mainly consists of an alphabetically arranged series of "Definitions, Principles and Explanatory Data," but is marred by quite a number of serious inaccuracies. Thus, austenite in steel is described as "a compound of  $\gamma$ -ferrite with iron carbide," and martensite as "consisting of a solid solution of (2%) carbon in iron which decomposes on slow cooling into ferrite and cementite." Again, a eutectoid is defined as a substance consisting of two or more components with a common melting-point, *e.g.*, pearlite, but then, curiously enough, the author goes on to state that it "differs from true eutectic in being formed from solid solution." It would indeed be most unfortunate if pearlite really melted during the heat treatment of steel.

Section II., consisting of some 260 pages, forms the major part of the book and is entitled "The Constituents of Iron and Steel." This Section deals mainly with analytical methods, prefaced by summaries of the physical constants of the elements, and preliminary paragraphs are devoted to briefly described methods of extraction, the general chemical properties of these elements and their influences on the properties of iron and steel.

Generally, the analytical methods described in Section II. are sound, as would be expected from the author's experiences in the various laboratories with which he has been associated, although some of the methods are open to criticism, and the stated limits of accuracy are wider than those usually expected. For instance, methods for sulphur (both gravimetric and volumetric) are described, where the expected accuracy is given as  $\pm 0.004\%$  for steels containing less than

0.10% of the element. In the gravimetric barium-sulphate process for sulphur the author favours the American method, where the iron is reduced by means of zinc prior to precipitation.

A notable and useful feature of this Section is the wide application of organic reagents and precipitants. In many instances the author advocates sulphuric-phosphoric acid mixtures as solvents and for creating the best conditions for oxidation, titration, &c., and there is little doubt that such mixtures serve very useful purposes.

The method for the determination of silicon in high-speed steels, whereby the tungsten is retained in solution as phospho-tungstic acid, has much to recommend it, and in the bismuthate method for manganese the substitution of ammonium persulphate for sodium bismuthate in the preliminary oxidation of the carbonaceous matter is an excellent and economical suggestion.

The thiocyanate method for iron, based on Bradbury and Edwards' work, for plain iron and steels is of interest, but the ordinary stannous-chloride method, using sodium or barium diphenylamine sulphonate as internal indicator, is equally satisfactory.

The author advocates fusion with sodium peroxide in the determination of chromium in all ferro-chromium alloys, since "decomposition in acids is not practicable on account of carbides," but is apparently unaware of the fact that the low-carbon (carbon-free) alloys are completely soluble in acids.

In the determination of cobalt, the  $\alpha$ -nitroso- $\beta$ -naphthol and cyanometric methods are described, but no mention is made of the sulphide process, which is quite satisfactory when nickel and copper are absent.

The author has, in the main, apparently concentrated on methods where practically all interfering elements are assumed to be present. Generally, this is a good principle, but in many instances it may lead to unnecessary complications; for instance, in the methods for the determination of copper in iron and steel he considers interfering elements such as chromium, tantalum, columbium, tin, molybdenum, tellurium, selenium and even cerium. Again, in regard to the determination of silicon, he almost gives one the impression that boron is a normal constituent in steel.

One wonders why, in a work on analytical chemistry, it should have been thought necessary to include descriptions of the blast-furnace and cupola processes for the production of cast iron, or of the several processes for the manufacture of steel.

In this Section there are a number of errors in regard to chemical nomenclature and formulæ, the latter having apparently been overlooked during the proof-reading. Thus, cerium ferride is given the formula  $\text{CeF}_{10}$  and orthosilicic acid  $\text{H}_4\text{Si}_2\text{O}_4$ . Manganic hydrate is associated with the formula  $\text{Mn}_2\text{O}_2(\text{OH})_2$ , which is of doubtful existence, and permanganic acid with the formula  $\text{H}_2\text{Mn}_2\text{O}_8$ .

In a table in Section II. dealing with the allotropes of iron, the author states that  $\alpha$ -iron is soft,  $\beta$ -iron is hard and that the hardness of  $\gamma$ -iron is between those of  $\alpha$  and  $\beta$ , views which can hardly be reconciled with fact and modern ideas.

A notable omission from Section II. is the lack of any reference to the determinations of oxygen, nitrogen and hydrogen in iron and steel, without which no modern work on the subject of ferrous analysis can be regarded as complete.

Section III. is devoted to the analysis of refractory materials, and involves some 20 pages only.

Notwithstanding the above criticisms, there is much excellent material in the book, but it is a work for the experienced metallurgical analyst rather than for the student.

As already indicated, most of the methods described are sound and

likely to yield reproducible results, in many cases of a higher order of accuracy than the author has indicated.

Even the experienced analyst will derive some benefit by reading the book, but the great pity is that the author did not confine his attention solely to the practice of metallurgical analysis without reference to theoretical, and often irrelevant, details, since otherwise the work would have made a strong appeal to both industrial and academic institutions.

The published price of the book (28s.) is high, compared with those of standard works of similar kind.

EDWIN GREGORY.

SISCO, F. T. *Modern Metallurgy for Engineers*. 8vo, pp. 426, New York, 1941: Pitman Publishing Corporation; London: Sir Isaac Pitman & Sons, Ltd. (Price 22s. 6d.)

In the preface to this book the author states that he made a conscientious effort to keep the text as elementary as possible and he has undoubtedly produced a well-written and easily understandable text book.

Unfortunately, the general arrangement is so bad that it detracts considerably from the value of the book. It is, for instance, somewhat disconcerting to find a chapter devoted to grey cast iron and malleable cast iron interposed between a chapter devoted to a consideration of carbon steel as an engineering material (Chapter 11) and another chapter (13) devoted to a consideration of low-alloy steels as engineering materials. Also one must turn to the end of Chapter 19, which is devoted to miscellaneous heavy non-ferrous alloys, before learning anything about sintered tungsten carbide tools, which one would certainly anticipate being described in Chapter 15 which is devoted to tool and die steels.

The book is, nevertheless, one that may with advantage be read by all engineers, although out of the twenty-one chapters eighteen are almost exclusively "steel" chapters.

The first seven chapters serve as a general introduction to the manufacture and heat treatment of iron and steel. Chapter 8 is devoted to a consideration of the significance of the static properties of metallic materials. The most instructive chapter in the whole book is number 9 and this should be read by all engineers with particular care because it describes so clearly the significance of the dynamic properties of metallic materials. There is nothing in this chapter that has not been published before, but the whole of the matter has never previously been so clearly brought together in one, comparatively speaking, short chapter. Chapter 21 is of equal importance as it gives a good general survey of creep and the general effect of temperature on physical properties.

Three chapters are devoted to non-ferrous metals, viz., Chapters 16, 17 and 18. These three chapters are, however, written in very general terms and should not be looked upon as anything more than a very brief introduction.

J. FERDINAND KAYSER.

## ORES—MINING AND TREATMENT

(Continued from pp. 88 A-89 A)

**Concentration of Manganese-Bearing Ore from the Stange Mine, Bland County, Va.** S. M. Shelton, M. M. Fine, J. B. Zadra and R. B. Fisher. (United States Bureau of Mines, Manganese Investigations No. 12, Apr., 1942, Report of Investigations No. 3633).

**Concentration of Manganese-Bearing Ore from the Mayfield Property, Van Horn, Tex.** J. B. Zadra, M. M. Fine, S. M. Shelton and T. L. Johnston. (United States Bureau of Mines, Manganese Investigations No. 13, Apr., 1942, Report of Investigations No. 3632).

**The Preparation and Beneficiation of the Ores of Eastern Germany.** K. Guthmann. (Stahl und Eisen, 1942, vol. 62, Feb. 26, pp. 182-183). The author gives information on the geology and value of the iron ores of Czechoslovakia and Poland and describes how they are roasted. The principal ore deposit in Czechoslovakia is the chamosite in the Prague-Pilsen silurian trough; it contains 28-35% of iron; it is roasted at 750-800° C. in cylindrical shaft furnaces 22 ft. high and 11 ft. in dia., the throughput being only 20 tons of crude ore per 24 hr. The principal mining centre of Poland is Czystochowa; the ore in this region contains 25-45% of iron; it is screened and roasted, and the screenings before and after roasting require sintering before smelting. In the Starachowice, Ostrowice and Warthenau districts the ores are roasted in circular shaft furnaces 15-25 ft. high. (An abridged English translation of this article appeared in Iron and Coal Trades Review, 1942, vol. 145, July 3, p. 393).

**Sponge Chromium.** C. G. Maier. (United States Bureau of Mines, 1942, Bulletin No. 436). The term "sponge chromium" in this paper refers to metallic chromium reduced under such conditions that the individual metallic crystals have grown to a size approaching or greater than the order of one micron. The author points out the advantages of producing metallic chromium from chromium chlorides rather than by the reduction of oxides. The chlorination of chromite ores and the production of sponge chromium from the chlorides are described and discussed in detail, and an investigation of special methods to obtain a product of high purity is described.

## REFRACTORY MATERIALS

(Continued from pp. 89 A-91 A)

**Conversion of Magnesite to Periclase.** B. L. Bailey. (Electrochemical Society, Apr., 1942, Preprint No. 81-28). The author



reports on some tests made on the conversion of magnesium carbonate to periclase by progressive calcination and the electrical fusion of the oxide. The calcining was done at temperatures in the 900–1650° C. range; the loss in weight and the rehydration gain after the sample had been exposed to the atmosphere for about 12 hr. were determined. The rehydration gain was found to drop sharply after calcining at 1200° C., and became practically negligible after 25 min. at 1650° C. A petrographic examination indicated that the magnesite was completely decomposed at 900° C. into an isotropic material which absorbs water fairly rapidly; this material is converted into periclase rapidly as the temperature passes 1200° C., and the conversion is practically complete at about 1300° C.

**The Linings of Large Basic Open-Hearth Tilting Furnaces.** A. Jackson. (Iron and Steel Institute, 1942, this Journal, Section I.). The author deals first with the problem of the linings of large basic open-hearth tilting furnaces from the viewpoint of lining stability when the furnace is tilted, particularly with regard to the lining on the charging side. Then two types of operation and the resultant methods of fettling are briefly outlined. The causes of excessive hearth wear are enumerated, and the resultant effects on the brickwork of the hearth and linings described. Further, the materials now being used for brickwork of the furnace body and for lining maintenance are discussed. Future prospects are briefly reviewed, and a brief summary of the brick consumption on two modern furnaces, from which over half a million tons of ingots had been cast, is given in an Appendix.

## FUEL

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(Continued from pp. 91 A–93 A)

**An Electrical Instrument for Determining the Dew-Point of Gases.** B. M. Thornton. (Engineering and Boiler House Review, 1942, vol. 56, July, pp. 66–69, 89). The author describes an electrical instrument, originally designed for determining the dew-point of flue gases from boilers, which is now being applied to the prevention of the corrosion of economisers, air heaters, steel flues, fan casings and chimneys. It is based on measurements of the change of the electrical resistance of a surface when dew is deposited.

**Pulverized Coal.** C. F. Herrington. (Steel, 1942, vol. 110, June 1, pp. 62–63, 98–100). The author discusses the following aspects of the use of pulverised coal for modern reheating furnaces: (a) Grinding, storing and transporting the coal; (b) burner design; (c) furnace design; (d) provision for ash; and (e) automatic control of grinding, fuel-air ratio, temperature and coal-feed.

## PRODUCTION OF IRON

(Continued from pp. 94 A-95 A)

**Blast-Furnace Air-Heating.** G. Auer. (Iron Age, 1942, vol. 149, Apr. 16, pp. 44-48; Apr. 23, pp. 43-48; Apr. 30, pp. 50-55, 109). The author considers the possibilities of using direct-fired tubular air-heaters for heating blast-furnace blast. The application of tubular units in which the heat is transferred by radiation and convection as in the petroleum industry is discussed in general terms, together with methods of calculating heat-transfer rates, with particular reference to the Stefan-Boltzmann formula. In the second part of the paper Hottel's and Egbert's methods of calculating the radiation of furnace gases and of determining the effect of changes in the proportions of the radiating and non-radiating components are explained, and reference is made to the addition of moist diluent gases to blast-furnace gas so as to reduce the flame temperature below the limit at which metal blast-heaters can be used. The design of tubular blast-heaters and the selection of suitable material for the stoves are also dealt with in this part. In the concluding part examples are given of (a) the calculation of the radiant heat-transfer rates for the roof, wall and shield-tubes in the design of a blast-heater, (b) the heat absorbed in the convection section, (c) the pressure drop of the air passing through the tubes, and (d) the draft loss for the flue gases.

**Desulphurizing at the Blast Furnace.** G. S. Evans. (Iron Age, 1942, vol. 149, Apr. 30, pp. 45-47). The author describes the equipment necessary for the efficient desulphurisation of molten pig iron with soda ash when tapping a large blast-furnace; one type is proposed for when the iron is required in ladles, and another for works where a pig-casting machine is used. The forms in which soda ash is sold are described.

**The Metallurgy of Acid-Resisting Iron-Silicon Alloys.** V. E. Vasilev and K. I. Vashenko. (Teoria i Praktika Metallurgii, 1938, No. 4, pp. 20-32). (In Russian). After reviewing the properties of high-silicon iron-silicon-carbon alloys containing 12-18% of silicon, the authors describe the manufacture of these alloys in reverberatory and open-hearth furnaces, giving details of the composition of the charge, the absorption of gases by the melt, and slags. The working of two typical charges is described in detail. An English translation of this paper is now available as No. 96 in the Translation Series of The Iron and Steel Institute.

**Open-Hearth Melting Stock Direct from Iron Ore.** (Blast Furnace and Steel Plant, 1942, vol. 30, Apr., pp. S-40-S-42). A rotary-furnace process is outlined by which nodules of low-carbon low-silicon iron can be produced direct from ore, the object being to obtain a substitute material for steel scrap which can be charged

in open-hearth furnaces. It is claimed that low-grade ores with only 25% of metallic iron can be successfully reduced in this manner. A drawing of the rotary furnace is presented, but no technical details of the process are given.

## FOUNDRY PRACTICE

(Continued from pp. 95 A-103 A)

**Mixing and Rotation of Cupola Charges.** E. Longden. (Iron and Steel, 1942, vol. 15, May, pp. 269-271; June, pp. 353-356). The author discusses the arranging of the composition and sequence of cupola charges so as to be able to produce metal of different specified compositions in one blowing period, and gives examples of how to calculate the gains and losses in the principal elements as charged into the cupola. In the second part of the paper he presents a series of charts and tables of analyses with a comprehensive index of different types of castings; these enable the desirable analysis for a casting of given thickness to be determined rapidly.

**Economical Alloying of Gray Cast Iron.** R. G. McElwee and T. E. Barlow. (Foundry, 1942, vol. 70, June, pp. 54-55, 141-146). The authors discuss methods of securing the most economical use of ferro-alloys and alloying elements in foundries making grey-iron castings. They suggest that sulphur should be kept below 0.12% and manganese controlled between 0.60% and 0.90% to minimise chill and thereby reduce the amount of alloying element required for chill regulation. Small amounts of either vanadium and titanium reduce chill when used as ladle additions, in spite of the fact that they are both strong carbide stabilisers; this has enabled combinations of alloying elements containing chromium, silicon and manganese to be developed which promote chill reduction and reduce the variations of structure while still maintaining their inherent stabilising effect.

**Casting Plow Parts and Pipe Fittings.** P. Dwyer. (Foundry, 1942, vol. 70, May, pp. 101-103, 194-197). The author describes, with numerous illustrations, the foundry practice at the works of Lynchburg Foundry Co., Lynchburg, Virginia, at which cast-iron plough parts and pipe fittings are made.

**Manufacture of High Test Cast Iron Crankshafts.** E. M. Currie and R. B. Templeton. (Iron Age, 1942, vol. 149, May 21, pp. 42-46). The authors compare the properties of crankshafts made of forged steel and of high-duty cast iron, with special reference to Meehanite, and give some information on the foundry practice for the production of Meehanite.

**Brake Drums.** O. Smalley. (Metals and Alloys, 1942, vol. 15, Feb., pp. 256-262; Mar., pp. 405-411; Apr., pp. 595-598). After a general discussion of the behaviour of cast-iron brake-drums of

automobiles the author describes dynamometer tests carried out on Meehanite, a molybdenum cast iron, a high-test cast iron and a nickel-chromium cast iron. Micrographs of the tested surfaces are reproduced. The Meehanite showed the least tendency to thermal cracking; no free ferrite and traces only of phosphide were visible, whilst the pearlite was in an exceedingly fine state. The iron containing 0.75% of molybdenum exhibited very good resistance to thermal cracks, but was comparatively easily scored; the micrographs in this case indicated that whilst large quantities of graphite might help to improve the resistance to thermal cracks, this is only true when the graphite is well distributed. The high-test iron contained total carbon 3.03% and silicon 2.09%. With this high silicon content the carbide is unstable at relatively low temperatures and decomposition to ferrite and graphite occurs. In the tests described the thermal cracks penetrated along the graphite flakes and the cracks filled up with iron oxide. The alloy cast iron tested contained total carbon 3.26%, silicon 1.92%, nickel 1.23% and chromium 0.25%. It did not have a good resistance to thermal cracking, but the cracks were less inclined to follow the graphite flakes than was the case with the high-silicon iron. Its resistance to scoring was very high.

**Navy Yard Foundry Develops Casting Technique.** P. Dwyer. (Foundry, 1942, vol. 70, June, pp. 50-53, 159, 160). The author describes the layout and plant at an American naval-yard foundry equipped for making heavy steel castings; the equipment includes a 50-ton acid open-hearth furnace and a 6-ton basic electric furnace. Some particulars of moulding-sand and core-sand mixtures are given.

**Production of Uniform Steel for a Light Castings Foundry.** C. H. Kain and L. W. Sanders. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, July 23, pp. 281-286, 292). The authors describe the technique employed at a foundry producing light castings in order to have molten steel ready at the periods when it is most wanted. The plant includes a basic-lined electric furnace and a Tropenas converter. This combination has two great advantages: (1) A wide range of scrap can be used in the electric furnace to produce a low-phosphorus, low-sulphur metal, the remelt from which can be used in conjunction with West Coast hematite in the Tropenas converter to produce steel with a phosphorus and sulphur content comparable with that of electric-arc furnace steel. (2) The electric furnace can be adjusted to produce a heat of steel at precise intervals, day and night, whilst the Tropenas converter can produce heats at high speed during peak casting periods.

**Converting an Iron Foundry to Make Steel Castings.** A. W. Gregg. (Foundry, 1942, vol. 70, June, pp. 58-59, 148-149). The author discusses the additions to plant and facilities which would be necessary to enable an iron foundry to undertake the production of steel castings.



**Clay Slurry Additions for Molding Sand Rebonding.** R. H. Mooney. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 940-950). The author describes the development at one of the plants of General Motors Corporation of equipment for preparing a clay slurry and adding this continuously to the moulding-sand system of the foundry for rebonding the sand. The equipment consists of a large clay storage hopper about 30 ft. above ground from which the clay is fed into a 200-gal. mixing tank with electrically-driven mixing paddles. The slurry passes through an  $\frac{1}{8}$ -in. mesh strainer at the bottom of the tank, down a pipe with a graduated plug-cock to control the flow into the continuous muller or mixer, where it enters the sand system. The advantages of using this equipment are discussed.

**Reproducibility of Tests of Foundry Sand.** S. Walker. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 789-817). The author describes an investigation carried out by the Foundry Sand Committee of the National Industrial Sand Association. The Committee attempted, with the co-operation of more than forty laboratories, to study what variations are to be expected because of differences in apparatus and testing technique. Three series of tests were carried out: (1) Identical samples of unbonded sand were tested to obtain sieve analyses; (2) about thirty portions of four master samples of unbonded samples were compared by sieve analysis; and (3) two groups of master samples of bonded sand were divided into portions and tested for fineness, strength, permeability and other properties. The results are given in detail. The author is of the opinion that tests applied to foundry sands are not reproducible with sufficient accuracy to permit the practical use of specifications involving small tolerances, and that the whole question of test procedure needs further study before uniform results from different laboratories can be expected.

**Steel Sand Preparation by the Wet Method.** H. Mason. (Transactions of the American Foundrymen's Association, 1942, vol. 49, June, pp. 1115-1129). The author describes the equipment installed at the works of the Symington Gould Corporation for the cleaning of castings. The sand is washed from the castings by a mixture of sand and water under pressure. This mixture, plus the sand removed, is run through a classifier; this separates the fines, which are rejected, from the remaining sand. The latter is returned to the foundry, where it is dried to less than 1% of moisture; it is then ready for use in facing sands and for cores.

**Casting 500-lb. Aerial Bombs.** (Iron Age, 1942, vol. 149, June 4, pp. 59-61). A description is given of the core-making and moulding for casting steel shells for 500-lb. bombs. The article appeared originally as Part II. of a paper entitled "The Foundry Industry and Air Warfare" (see p. 49 A).

**Elimination of Dust and Noise in the Foundry.** F. E. Grütz-macher. (Giesserei, 1942, vol. 29, Apr. 17, pp. 129-136). The

author describes and illustrates methods adopted in Germany and America for lighting and ventilating foundries and for dealing with dust, fumes and noise.

**Combating Noise, Dust and Smoke in the Foundry.** H. Schrader. (Giesserei, 1942, vol. 29, May 29, pp. 186-189). The author makes recommendations on the design of moulding-machine foundations, conveyors, sand-bunkers, core-blowers, drying ovens and grinding and fettling shops with special reference to the prevention of unnecessary noise, dust and fumes.

## PRODUCTION OF STEEL

(Continued from pp. 103 A-105 A)

**The French Iron and Steel Industry.** (Iron and Coal Trades Review, 1942, vol. 145, June 26, pp. 349-350). An outline is presented of the present position of the French iron and steel industry under German domination. The two major administrative organisations in the industry, the Comité des Forges de France and the Comptoir Sidérurgique de France, were dissolved by November, 1940.

**Dominion Foundries and Steel, Ltd.** T. J. Ess. (Iron and Steel Engineer, 1942, vol. 19, Apr., pp. 37-47). An illustrated description is given of the works of Dominion Foundries and Steel, Ltd., at Hamilton, Ontario. The plant comprises four 60-ton basic open-hearth furnaces and five arc furnaces of from  $1\frac{1}{2}$  to 50 tons with plate and hot-strip mills, a 34-in. reversing cold-strip mill and a tension mill with finishing departments. There are also large steel casting and forging departments.

**Steel Company of Canada, Ltd.** T. J. Ess. (Iron and Steel Engineer, 1942, vol. 19, Apr., pp. 69-84). A comprehensive illustrated description is given of the iron and steel works, rolling mills and finishing departments of the Steel Company of Canada, Ltd., at Hamilton, Ontario, where there are two 40-oven batteries of coke-ovens, three blast-furnaces, five 175-ton and four 100-ton open-hearth furnaces, rolling mills for blooms, billets, plates, sheets and bars, and finishing departments.

**Maintenance of Instruments and Controls in the Steel Plant.** R. A. Weikel. (Iron and Steel Engineer, 1942, vol. 19, Apr., pp. 115-118). The author outlines the organisation of an instrument department for a steelworks, dealing especially with the training of men, considerations governing the selection of an instrument for a particular purpose, and the positioning and maintenance of instruments.

**The Duplex Process for the Manufacture of Basic Open Hearth Steel.** H. B. Emerick and S. Feigenbaum. (American Institute of Mining and Metallurgical Engineers: Blast Furnace and Steel Plant, 1942, vol. 30, May, pp. 521-531). The authors review the

development of the duplex process of steelmaking in the United States, making numerous references to the literature. The economic aspect is dealt with first, and its flexibility to suit changing conditions of the heavy steel scrap market is pointed out as one of its particular advantages. The operation of the process is then described in detail. Control of the blown-metal temperature is highly desirable, as too high a temperature produces a high nitrogen content, and sometimes results in incomplete oxidation of the silicon. In tilting-furnace operation it is advantageous to have a pool of metal in the furnace on tapping rather than to work the "dry bottom" practice. In the authors' opinion the amount of metal in the pool should not exceed about 10% of the amount of metal tapped. The oxidation of manganese which occurs during the blowing deprives the duplex process of its principal source of manganese; this low residual manganese (0.04–0.10%) has been cited as a serious metallurgical drawback to the duplex process, for manganese is presumed to protect the bath from over-oxidation. In actual fact this applies only when the carbon is quite low (under about 0.10%), as above this value the carbon itself plays the decisive rôle in controlling the oxygen content. The relatively higher degree of oxidation of the bath in duplex operation is advantageous in the production of rimming steels, but killed steels of high quality can also be readily produced by applying suitable deoxidation practice.

**The Theory of the Electric Arc Furnace. I. and II.** P. Drossbach. (*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1940, vol. 46, Nov., pp. 643–646; Dec., pp. 668–669). In the first part of this mathematical treatise the author develops equations for calculating the growth and extent of the melting zone of an electric arc furnace and the distribution of energy in the furnace under ideal conditions, assuming that the downward flowing molten metal is not superheated. In the second part formulæ are developed which take into account the superheating of the molten metal at the boundary of the melting zone.

**The Effect of Manganese on the Desulphurizing Power of Calcium Silicates.** F. W. Scott and T. L. Joseph. (*Blast Furnace and Steel Plant*, 1942, vol. 30, Apr., pp. 425–430; May, pp. 532–535, 541). The authors report on their laboratory investigation of the effect of manganese in the metal and of manganous oxide in the slag on the desulphurising power of calcium silicates in equilibrium with metal at various temperatures. The experiments were performed in the rotating furnace previously described (*see* p. 104 A). The basicity of the slags was restricted to those which are molten between 1550° and 1675° C. Simple slags were formed from mixtures of pure lime and pure silica to form the following silicates:  $\text{CaO} \cdot 2\text{SiO}_2$ ;  $\text{CaO} \cdot \text{SiO}_2$ ;  $3\text{CaO} \cdot 2\text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$ . The results are presented in tables and several series of curves in which the manganese content of the metal is plotted against the sulphur distribution coefficient (the sulphur content of the slag divided by

that of the metal). The data obtained led to the following conclusions: (1) Manganese in the metal increases the desulphurising power of calcium silicate slags; with the same slag basicity and the same manganese concentration in the metal, higher temperatures promote greater desulphurisation; this tendency is most pronounced with increasing amounts of manganese in the metal and is attributed to a decrease in the iron oxide in the slag. (2) The effect of temperature upon the sulphur distribution coefficient is negligible when the basicity and the MnO in the slag are constant. An increase in the MnO in the slag is accompanied by an increase in desulphurising power, which is more pronounced in basic slag; a given increase of MnO in the slag is more effective in aiding desulphurisation when the slag is most basic, because it results in a proportionately greater increase in the manganese in the metal. (3) For a given range of manganese, increasing the basicity of the slag lowers the numerical value of the sulphur distribution coefficient. (4) When the lime/silica ratio is equal to or greater than unity, the sulphur-distribution constant changes less for a given manganese variation in the metal.

## REHEATING FURNACES

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(Continued from p. 105 A)

**Forge Furnace Design.** F. S. Bloom. (American Gas Association: Heat Treating and Forging, 1942, vol. 18, Apr., pp. 189-190). The author presents curves showing the differences between the temperatures at the surface and centre of 6-in. and 10-in. square billets and of 13-in. and 20-in. round billets in the course of heating them up to 2250° F. in a reheating furnace fired with natural gas; these curves show that the differences are less than is generally expected, and that the rates of heat absorption at a constant furnace temperature are greater than expected. He deduces that the rate of heat absorption for steel is as high as 100,000 B.Th.U. per sq. ft. per hr., and shows that in designing forging furnaces to supply sufficient heat to heat up steel at this rate unusually tall furnaces would be required.

**Increasing the Efficiency of the Forging Furnace.** A. F. Macconochie. (Steel, 1942, vol. 110, May 18, pp. 76-80, 121). The author discusses the requirements of reheating furnaces for forgings and how these affect design. He distinguishes between the burning and overheating of forgings, the former meaning heating to a temperature at which the more fusible elements melt and run, leaving cavities between the grains, and the latter meaning heating to temperatures at which grain growth takes place. In determining the capacity of a batch-type forging furnace a basis to work on is that 50-100 lb. of steel can be heated to forging temperature at 1 sq. ft. per hr.



## FORGING, STAMPING AND DRAWING

(Continued from pp. 105 A-106 A)

**The Forgeability of Metals.** O. W. Ellis. (Engineering Institute of Canada and American Society for Metals, Joint Meeting : Engineering Journal, 1941, Oct., Reprint). The author reviews experimental work on the forgeability of metals with reference to the properties of the materials, the technique required and the results obtained in die-forging and in free-forging. As an example, the forging of an eccentric cam produced in steel and in aluminium alloy of medium forgeability is discussed and an estimate is made of the comparative cost of manufacture.

**Forgings and Forging Practice.** A. F. Macconochie. (Steel, 1942, vol. 110, June 29, pp. 56-58). The author discusses forging practice, dealing with the effect of using too light a hammer and making up for the deficiency in mass by increasing the velocity, how to reduce trimming costs, and the finishing of forgings by hot-coining so as to reduce machining costs.

**Forging 90-mm. Shells on Self-Contained Presses.** (Iron Age, 1942, vol. 149, June 18, pp. 47-50). A process of forging 90-mm. shells in two presses at a rate of 3000 shells in 24 hr. is described and illustrated. Instead of using a water hydraulic system with a battery of pumps and a weighted accumulator, these presses are individually driven with reversible oil hydraulic pumps with valveless closed hydraulic circuits. The shell billets are cut 10 in. long and heated to 2170° F. The first press pierces the billet, and the second press "bottoms" the cavity and draws the pierced forging to the proper length and cross-section.

**Are Sleeves Necessary for Redrawing Shells?** C. W. Hinman. (Heat Treating and Forging, 1942, vol. 18, Apr., pp. 178-181). The author describes the operation of redrawing cylindrical shells or cups to cups of smaller diameter and increased height, and discusses the advantages and disadvantages of using a sleeve round the redrawing punch.

**Forging Dies.** P. Patek. (Heat Treating and Forging, 1942, vol. 18, Apr., pp. 169-171). The author discusses factors influencing the design of dies for making depressions in forgings, and presents data to facilitate the calculation of the correct slope of die walls and the radius of the die nose.

**Stretch-Forming Contoured Sheet Metal Aircraft Parts.** T. H. Hazlett and M. M. Rockwell. (Iron Age, 1942, vol. 149, June 4, pp. 49-53). The authors describe the development of forming machines which combine stretching and pressing in a manner suitable for the rapid production of parts with double-curvature contours of large radius, such as cowling panels and aircraft engine nacelles. Stretch-forming usually consists of clamping the sheet-

metal blank along two opposite edges and pressing on the centre with a head of the desired shape without having a corresponding female die; the metal is, of course, stretched into the plastic range.

**A Method for Measuring the Contours of Wire Drawing Dies.** L. B. Barker. (Wire and Wire Products, 1942, vol. 17, Apr., pp. 187-189). The author describes a method of checking the contours of wire-drawing dies. This consists of making a Wood's metal cast in the die to be checked by a technique which allows the cast to be withdrawn so that one side of it provides a full contour of the bearing surface of the die. The cast or model is then examined in a bench-type comparator fitted with special viewing screens and accessories.

**Carbide Drawing Dies.** J. R. Longwell. (Canadian Metals and Metallurgical Industries, 1942, vol. 5, May, pp. 147-148). The author makes recommendations on the use and maintenance of cemented carbide dies for drawing wire and special shapes.

## ROLLING-MILL PRACTICE

(Continued from pp. 59 A-60 A)

**Steel Mill Applications of Rectifiers.** M. J. Leding. (Iron Age, 1942, vol. 149, Apr. 9, p. 59). The author briefly reviews the advantages of using Ignitron rectifiers instead of motor-generator sets for obtaining direct current for mill motors.

**Economical Rolling.** A. E. Lendl. (Iron and Steel, 1942, vol. 15, July, pp. 378-382). The author gives details of the costs, at a continental steelworks, of operating a reheating furnace for heating  $3\frac{1}{8}$  in. sq. billets at 14.1 tons per hr. and of rolling these down to  $\frac{5}{8}$  in. rounds in a six-stand 13 in. roughing mill and a six-stand 13 in. finishing mill.

**The Temper Mill.** T. B. Montgomery. (Iron and Steel Engineer, 1942, vol. 19, Apr., pp. 90-100). The author discusses the theory of temper-mill rolling (or the continuous finish-rolling of steel strip under tension) with special reference to the calculation of power requirements and to methods of control.

**Cold-Rolling—A Heat Problem.** G. Reimer. (Iron and Steel Institute, 1942, Translation Series, No. 97). An English Translation is presented of the author's paper on thermal-conductivity problems in connection with the cooling of rolls used for cold-rolling wide steel strip. This appeared originally in Stahl und Eisen, 1939, vol. 59, Oct. 12, pp. 1134-1136 (see Journ. I and S.I., 1940, No. I., p. 88 A).

**The Röchling Wide Strip Mill.** (Sheet Metal Industries, 1942, vol. 16, July, pp. 965-966). An abridged English translation of D. Timmermann's paper which appeared in Stahl und Eisen, 1942, vol. 62, Feb. 5, pp. 109-114, is presented. In this a description of the Broemel new wide strip mill at the Röchling steelworks at Völklingen is given. (See p. 14 A).

**Developments in Strip-Steel Finishing Lines.** R. J. Wean. (Steel, 1942, vol. 110, Apr. 6, pp. 85-88). A brief illustrated description is given of some recently erected American strip-mill equipment which can be used for more than one purpose. One example is a combination slitting and shearing line consisting of a coil holder, slitter, reel, flying shear, belt conveyor and piler, arranged to receive material in coils and either to slit it into multiple widths and recoil it or to shear it into cut lengths and pile it. The author observes a trend towards the use of hydraulic power for the auxiliary movements of reels and uncoilers.

**New Plant which Has Been Designed for Improving the Surface Quality and Gauge Accuracy of Steel Strip.** (Sheet Metal Industries, 1942, vol. 16, May, pp. 604-606). A brief illustrated description is given of the rolling-mill plant at the B. M. Rolling Mills, Ltd., Birmingham, where cold-rolled steel strip from  $\frac{3}{8}$  in. to  $9\frac{1}{2}$  in. wide and from 0.005 in. to  $\frac{3}{8}$  in. thick is produced. The heavier material is broken down in a two-high 12-in. stand and finished in a four-high 12-in. stand with working rolls  $5\frac{1}{2}$  in. in dia. and backing rolls  $12\frac{3}{4}$  in. in dia. The shape of both the working and the backing roll barrels is controlled by the cooling medium circulated by means of pads pressing lightly on the roll faces.

## PYROMETRY

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(Continued from p. 60 A)

**Pigment Paints and Pigment "Pencils" for the Measurement of Temperatures between 40° and 650° C.** K. Guthmann. (Stahl und Eisen, 1942, vol. 62, June 4, pp. 477-482). The author discusses the possibilities and technique of the application of "Thermocolor" pigments for the measurement of temperatures between 40° and 650° C. These pigments, which are patented in Germany, contain complex salts of various metals, the colour of which changes at definite temperatures owing to oxidation or to the splitting off of water, carbon dioxide or ammonia. If the temperature distribution over a larger surface area has to be measured, the pigments are applied in the form of paint and spread over the surface with the aid of a brush or, for more intricate shapes, a spraying pistol. For the measurement of the temperature of small areas the pigments can be used in the form of "pencils," of wax-like consistency, with which lines are drawn over the places the temperature of which has to be determined. Particularly interesting applications of Thermocolors are for the control of the temperature distribution during welding and soldering, and for the determination of frictional heat in machine parts.

## HEAT TREATMENT

(Continued from pp. 106 A-108 A)

**The Case Hardening of Low Carbon Steel.** D. W. Kinnaird. (Overseas Engineer, 1942, vol. 15, July, pp. 209-212, 215, 208). The author reviews methods of case-hardening low-carbon steel from the designer's point of view, describing the refining of the core structure, local or selective case-hardening and suitable instructions for insertion in drawings.

**Salt Baths.** R. C. Stewart. (Canadian Metals and Metallurgical Industries, 1942, vol. 5, May, pp. 130-133, 139). The author describes the theory and practice of case-hardening with salt baths. To accelerate the action of the molten cyanide, sodium fluoride or chloride is added. The case obtained in accelerated baths has far more carbon and far less nitride than that obtained in cyanide alone, the amount of nitrogen at the surface being only about 20% of that obtained with cyanide alone. A carbon top or cover is put over activated baths to prevent fuming, to reduce heat losses by radiation and to prevent excessive oxidation of cyanide in contact with the air sweeping over the bath surface. The hardening of alloy steels, malleable iron and high-speed steel in salt baths is dealt with briefly.

**Electrode-Type Salt-Bath Tool-Hardening Furnaces.** (Engineering, 1942, vol. 154, July 10, pp. 27-28). An illustrated description is given of a set of three electric furnaces for the heat treatment of high-speed steel tools. One furnace is rated at 18 kW. for preheating temperatures up to about 1000° C.; the second is a high-temperature furnace of 37.5 kW. for heating to 1350-1400° C.; the third furnace is a low-temperature one for hot quenching. The baths of the furnaces are triangular in section with the three main electrodes at the corners.

**Practical Gas Carburising.** I. Stewart. (Iron and Steel, 1942, vol. 15, May, pp. 279-281; June, pp. 373-375). The author traces the development of gas carburising and explains the fundamental principle on which all modern gas carburising is based, namely, the introduction of a volatile hydrocarbon to the furnace atmosphere, so diluted as to provide on decomposition the amount of carbon desired at the surface of the steel. The suitability of reducing, inert and oxidising gases as diluent gases and the choice of a volatile hydrocarbon are discussed. In the second part the importance of dehydration of the carburising gas mixture, the design and operation of furnaces and the advantages of gas carburising are dealt with.

**Oxyacetylene Flame Hardening.** J. G. Magrath. (Machinist, 1942, vol. 86, Apr. 4, pp. 1317-1319; Apr. 18, pp. 8-11; May 23, pp. 54-57; June 13, pp. 107-109; June 20, pp. 178-180; June 27, pp. 217-219). Continuation of a series of articles (see Journ. I.



and S.I., 1942, No. 1., p. 235 A). In Part 13 the equipment and technique for the flame-hardening of large cylindrical surfaces such as shafting, rolls, cylinders and cylinder liners are described and illustrated. Part 14 is devoted to the equipment and procedure for flame-hardening smaller circular and cylindrical parts in which the parts are spun and the flame is applied externally or internally. In Part 15 equipment for flame-hardening small and very large gear teeth is described and illustrated and details are given of hardness surveys on cross-sections of teeth hardened in this manner. In Parts 16 and 17 the special equipment for flame-hardening sprockets, screw-threads, worm wheels, sheaves and miscellaneous shapes is described. Part 18, which concludes the series, covers the flame-hardening of curved surfaces of unusual shape.

**Furnaces for Substitute "66" and "94."** (Wild-Barfield Heat-Treatment Journal, 1942, vol. 4, Mar.-June, pp. 72-78). The properties of two classes of tool steel referred to as "66" and "94" are briefly discussed. These contain about 6% and 9% of molybdenum and 6% and 4% of tungsten respectively, and are being extensively used as substitutes for 18% tungsten tool steels. Descriptions are then given of suitable furnace installations for preheating, hardening and tempering the substitute steels, special attention being given to molten salt baths in conjunction with electrically heated furnaces of the dry type.

## WELDING AND CUTTING

(Continued from pp. 108 A-111 A)

**The Spot Welding of N-A-X High-Tensile Steel.** W. F. Hess and C. R. Schroder. (Welding Journal, 1942, vol. 21, Apr., pp. 203-S-208-S). The authors report on an investigation of the properties of spot-welds in a low-alloy high-tensile steel sheet 0.040 in. thick known as "N-A-X High-Tensile Steel" containing carbon 0.14%, silicon 0.84%, chromium 0.57% and zirconium 0.11%. It has been found that brittle spot-welds in this sheet can be successfully toughened by a brief post welding treatment in the welding machine. The optimum conditions of treatment consisted of allowing a sufficient time interval between the passage of the welding and heat-treatment currents for the weld to cool to form a martensitic structure, and adjusting the second current application so as to produce a tempering temperature just below the critical point. Under the conditions of this investigation the best results were obtained by passing six cycles of welding current and allowing a time interval equivalent to 14 cycles to elapse before applying the heat-treatment current.

**Welding 18-8 Stainless Steel.** (Canadian Metals and Metallurgical Industries, 1942, vol. 5, May, pp. 145-146). A brief

description is given of the technique for the oxy-acetylene welding of stainless steel sheet.

**Welding the Stainless Steels.** H. S. Marquand. (Welding, 1942, vol. 10, Mar., pp. 35-37; Apr., pp. 57-59; May, p. 79). The author discusses the weldability of the following types of stainless steel: (a) Straight chromium hardenable steels with less than 16% of chromium; (b) non-hardenable ferritic straight chromium steels with more than 15% of chromium; and (c) austenitic chromium-nickel steels. He describes the preparation of joints and the procedures to follow for the electric and oxy-acetylene welding of these steels.

**Flash Butt Welding of High Speed Steel Tips to Mild Steel, Circular Blanks for Side and Face Milling Cutters.** H. E. Lardge. (Transactions of the Institute of Welding, 1942, vol. 5, Jan., p. 30; Machine Shop Magazine, 1942, vol. 3, July, pp. 50-51). The author describes the flash butt-welding of fifteen high-speed steel tips measuring  $\frac{5}{8} \times \frac{5}{8} \times \frac{1}{2}$  in. on to a mild-steel blank 4 in. in dia.  $\times \frac{1}{2}$  in. thick. The welding was done on a hand-operated 20-kVA. flash butt-welder. Milling cutters prepared in this way have given excellent service on magnesium castings.

**Manual Atomic Hydrogen Welding of Tool Steels.** C. H. Speakman. (Steel, 1942, vol. 110, May 18, pp. 86-88, 125). The author describes and illustrates some repair jobs that have been successfully carried out by manual atomic-hydrogen welding. These relate to die plates, punches, blanking dies, milling cutters and broaches—all tool steels. The use of this equipment by a skilled welder has resulted in very great savings.

**The Effect of Preheating Temperature upon Shrinkage Stresses in Welded High-Tensile Steel Plates.** R. W. Leutwiler, jun. (Welding Journal, 1942, vol. 21, Apr., pp. 198-S-203-S). The author reports on an investigation of the effect of preheating on the distortion and residual stresses after subsequent welding of specimens of  $\frac{3}{8}$ -in. plate of high-tensile steel containing carbon 0.09% and nickel 0.63%. The preheating was carried out for 15 min. at temperatures rising from 0° C. in 50° stages to 400° C. Six pairs of gauge-marks 15 in. apart were made on the test plate, which measured 18  $\times$  6 in. The pairs of marks were spaced 1 in. apart. A single bead of weld metal was deposited along one of the long edges, and the distances between the gauge-marks were accurately measured before preheating and after welding. The curvature caused by distortion was also measured. From the data obtained it was found that: (1) Preheating the plate at 200° C. reduced the distortion to approximately 65% of that which occurred when the plate was not preheated; (2) preheating the plate at 200° C. reduced the residual stresses occurring in an unpreheated plate by about 73%; and (3) to obtain the maximum benefit of preheating, the minimum preheating temperature should be 200° C.

**Static Tests of Fillet and Plug Welds.** W. Spraragen and G. E. Clausen. (Welding Journal, 1942, vol. 21, Apr., pp. 161-S-197-S).

The authors review the literature from 1931 to January 1, 1940, on static tests on fillet and plug welds including stress distribution and mode of failure.

**The Testing of Welds.** H. N. Pemberton. (North-East Coast Institution of Engineers and Shipbuilders : Welding, 1942, vol. 10, June, pp. 99-104 ; July, pp. 131-133). The author reviews methods of testing welds and the value of the data obtained by them. From a study of available fatigue research data he draws the following conclusions : (1) Heat treatment has practically no effect on fatigue endurance ; (2) within the usual commercial tensile limits for mild-steel plate, the grade of plate has no appreciable effect on the fatigue endurance of the weld ; (3) the highest class of butt-weld possesses double the fatigue endurance (under direct stress) of that obtained in structural welds ; (4) bending fatigue tests are specially sensitive to surface conditions ; (5) for ordinary structural welds bending fatigue tests give higher results than direct stress tests ; (6) the main source of danger in fatigue is lack of fusion at the weld junctions ; (7) there is no evidence that an unrefined layer of welded metal in a butt-weld decreases fatigue endurance ; and (8) there is no pronounced difference in the fatigue endurance of specimens of various thicknesses up to 3 in. thick. Fatigue tests on fillet-welds show that, in general, the highest quality of fillet-weld is much weaker than the butt-weld. Tensile, bend and notched-bar impact tests as well as non-destructive tests by X-rays and magnetic methods are also dealt with. In the author's opinion, no matter what system of routine and special testing is adopted, the greatest safeguard of weld quality is to be found in works supervision of all the practical details comprising welding procedure.

**Electric Arc Welding Plant and Equipment.** (British Standards Institution, No. 638-1941).

## PROPERTIES AND TESTS

(Continued from pp. 117 A-123 A)

**Tensile and Compressive Properties of some Stainless-Steel Sheets.** C. S. Aitchison, W. Ramberg, L. B. Tuckerman and H. L. Whittemore. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, Apr., pp. 499-567). The authors report on an investigation of the tensile and compressive strengths of 17/7 and 18/7 chromium-nickel stainless-steel sheets in thicknesses from 0.01 to 0.06 in. after various degrees of cold-reduction up to 50%. These steels are commercially available in the United States and are particularly suitable for aircraft structures. The compressive tests were made with packs of sheets cemented together with fused shellac by a method developed at the National Bureau of Standards. For annealed sheet the stress-strain curves and the yield strengths

from both tensile and pack compressive tests were about the same. For cold-reduced sheet the tensile stress-strain curves for longitudinal specimens differed in shape from the tensile stress-strain curves for transverse specimens, but the yield strengths were about the same. With comparable cold-reduction, the tensile strengths and the tensile and compressive yield strengths were about the same for all thicknesses of sheet investigated. Stress-relieving increased the tensile and compressive yield strengths in both the longitudinal and transverse directions; this effect was more marked the greater the amount of cold reduction.

**"Dead" Steel.** B. Thomas. (Metallurgia, 1942, vol. 26, June, pp. 55-56). The author cites an example of a 0.50% carbon steel which occasionally failed to respond to heat treatment and became known as "dead" steel. Normally the steel was forged out into plates measuring approximately  $11 \times 7 \times 0.130$  in., and these were hardened by quenching in fused salts at  $800-820^{\circ}\text{C}$ .; a tempering treatment at  $240-300^{\circ}\text{C}$ . followed. The desired hardness was 500-550 Brinell, but with the "dead" steels only 250-300 Brinell could be obtained. The trouble was eventually traced, by tests which are described, to the rolling of the original ingot at too high a temperature.

**Metallurgical Aspects of Gear Failures.** I. Stewart. (Mechanical World, 1942, vol. 111, June 5, pp. 509-511). The author discusses several examples of gear-tooth failures, dealing with the difficulty of tracing the causes. He points out the advantages of hard chromium plating for cylinder bores, cylinder liners, crankshafts and gauges, and suggests that in addition to providing an ideal surface for lubrication with a uniformity of hardness, the hard chromium possesses a fine homogeneous crystal structure ideal for wear resistance. The author suggests that, given a good lubricating surface and a homogeneous crystal structure, the significance of hardness is of minor importance. In support of this some data from Amsler wear tests on case-hardened and on siliconised steel are presented; from these it is seen that, although the former was much harder than the latter, the siliconised steel exhibited less wear.

**Metal Structure Phenomena under Tensile and Reversed Stresses.** A. Thum and C. Petersen. (Zeitschrift für Metallkunde, 1941, vol. 33, July, pp. 249-259). From the results of microscopical and X-ray investigations the authors developed a theory for the phenomena occurring in a metal subjected to tensile and reversed stresses. They show that even under quite small reversed stresses sub-microscopic cracks occur, the effect of which, as determined by X-ray stress measurements, is to produce an apparent increase in the elastic modulus; the explanation of this is that, after the sub-microscopic cracks have formed, there is no load on the material lying between them and there is no elongation of this material on repeating the stress on the test-piece. In this state the repetition of the same stress causes only a reduced elongation of the crystal



lattice at the surface, so that the elastic modulus calculated on this basis is greater than that of the material in its original state. The authors also discuss the inception and enlargement of these cracks in fatigue testing, as well as skin effects, notch sensitivity and initial stabilisation of the structure by low stresses repeated a great number of times.

**Properties of the New NE (National Emergency) Alloy Steels.** (Steel, 1942, vol. 110, June 8, pp. 66-69). A series of curves is presented compiled from end-quench hardenability tests on a number of high-manganese molybdenum steels and high-manganese chromium-nickel-molybdenum steels. These steels are recommended as substitutes for those with higher contents of alloying elements and have been given "N.E." (National Emergency) specification numbers by the War Production Board in the United States.

**Machinability of Steel and Malleable-Iron Castings.** (Machinery, 1942, vol. 61, July 2, pp. 18-20). In this article on factors affecting the machinability of castings the influence of selenium, sulphur, columbium, zirconium, manganese and bismuth on austenitic steels is dealt with first. Recent work indicates that the addition of small amounts of bismuth increases the machinability of stainless steels without any detrimental effects. Tests on the influence of the various deoxidisers used on the machinability in turning operations of free-cutting steels revealed that the machinability rating decreased in the following order of deoxidisers used: manganese, chromium, silicon, zirconium, aluminium, vanadium and titanium. For production work on malleable castings, iron with a tensile strength of about 20 tons per sq. in. and with 7% elongation on 2 in. gives the maximum machinability.

**Machinability of Ferrous Castings.** (Machinery, 1942, vol. 60, June 25, pp. 609-610). After a brief review of methods of measuring machinability, information is given on how the machinability of cast iron is affected by changes in the amounts of the following constituent elements, namely, silicon, manganese, sulphur, phosphorus, graphitic carbon, combined carbon, nickel, chromium, molybdenum, copper, zirconium, titanium and vanadium.

**Permanent Magnets.** J. H. Goss. (Metals and Alloys, 1942, vol. 15, Apr., pp. 576-582). The author describes the methods employed at the works of the General Electric Co. for manufacturing permanent magnets of chromium steel, tungsten steel and Alnico (iron alloyed with aluminium, nickel and cobalt). Alnico magnets can only be made by (a) the sintering or powder metallurgy process, or (b) casting and grinding. The casting technique has a pronounced influence on the magnetic properties, so that the selection of the proper furnace and control equipment is very important. The induction furnace has been found excellent for this purpose. The development of the equipment at the above works and the manufacture of Alnico magnets for watt-hour meters are briefly described with several illustrations.

**Cold-Deformed Manganese Steel as a New Material for Magnets.** W. Jellinghaus. (Iron and Steel Institute, 1942, Translation Series No. 98). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Aug., pp. 99-101. (See p. 27 A).

**Mechanics of Creep for Structural Analysis.** J. Marin. (Proceedings of the American Society of Civil Engineers, 1942, vol. 68, May, pp. 719-735). In this mathematical treatise the author develops a theory for determining the influence of creep at normal temperature as a factor in structural design. A theory for stresses and deflections in members subject to bending is developed, and the values are compared with creep-test results; theories are then derived for the analysis of statically indeterminate structures in cases where creep is present.

**The Physical Properties of Materials for Steam Power Plants.** F. J. Cowlin. (Rugby Engineering Society: English Electric Journal, 1942, vol. 10, June, pp. 121-127). The author reviews recently discovered facts relating to the properties of steel at different temperatures, particularly creep. He describes some of the creep-testing equipment at the National Physical Laboratory and at the Westinghouse Electric and Manufacturing Co. at Pittsburgh. The photo-elastic method of studying stress distribution in models of celluloid or resin compounds is also explained, and the fields open for further investigation are dealt with briefly.

**The Influence of Alloying Elements on the Tensile Strength and Creep Strength of Heat-Treated Steels.** W. Holtmann. (Mitteilungen der Kohle- und Eisenforschung G.m.b.H.: Stahl und Eisen, 1942, vol. 62, Jan. 8, pp. 32-35). The author reports on an investigation of the effect of the carbon content on the tensile and creep properties at 20°, 500° and 550° C. of steels alloyed with vanadium and molybdenum, and reviews the work of other investigators on similar steels. The results are shown in an unusual way by curves drawn through points of approximately equal creep strength, which are plotted on graphs with the carbon contents as ordinates and the molybdenum or vanadium contents as abscissæ. The contour diagram of the creep strength of vanadium steels shows an extended region in which a creep strength in excess of 20 kg. per sq. mm. at 500° C. is encountered. This region extends from about carbon 0.05% and vanadium 1.2% to carbon 0.3% and vanadium 3.0%. Near the borders of this region a more or less rapid decline in creep is registered, whilst a line of maximum creep strength traverses the length of the region. This "summit line" is seen to extend without change in direction beyond the field of high creep strength into the regions of lower creep strength. A similar line of maximum creep strength is seen in the molybdenum-carbon creep strength diagram. In this case the line of highest creep strength extends from carbon 0.02% and molybdenum 1.5% to approximately carbon 0.35% and molybdenum 5.3%. When these summit lines are shown on

the same graph as limit lines separating the regions of complete transformation from that in which the  $\alpha \rightarrow \gamma$  transformation is incomplete or absent, it is seen that they are close together and practically parallel. If, for the sake of simplification, it were permissible to assume that these two lines coincided, the following interrelationship between creep strength, tensile strength and structure could be established: In the steels ranged to the left of the limit line, consisting of a mixture of martensite and ferrite, the diminution in critical cooling speed caused by an increase in carbon and molybdenum or vanadium content results in a disappearance of the ferrite, and thus leads to a considerable increase in creep strength and tensile strength.

**Review of Recent Research into the Influence of Vanadium and Molybdenum upon the Creep Strength.** D. W. Rudorff. (Metallurgia, 1942, vol. 26, June, pp. 43-46). The author reviews recent work on the influence of vanadium and molybdenum on the creep strength of heat-treated steels, basing his information on a paper by Holtmann. (See preceding abstract).

**Copper-Bearing Steel for Heavy Fabrication. Parts I. and II.** F. Eberle. (Metals and Alloys, 1942, vol. 15, Apr., pp. 588-594; May, pp. 758-761). The author describes an investigation of the weldability and forging properties of copper-bearing high-tensile steel plate containing 0.26% of copper. It had previously been thought necessary to limit the copper content of steel plate for high-pressure boiler drums to 0.18%, and that for the drum-ends to 0.12%, owing to the danger of crack formation in the bending and flanging processes. The weldability of the test-pieces was found to be quite satisfactory. Forging tests on pieces  $12 \times 2 \times 1\frac{1}{4}$  in. were carried out after heating under severe and under normal conditions. The severe conditions consisted of heating to 2000° F. and holding for 4 hr. In this case, after forging down to half the original thickness and bending through 180°, numerous shallow surface tears developed. For forging tests under normal conditions the test-pieces had a  $1\frac{1}{4}$ -in. dia. hole in the centre and, after holding at 2000° F. for  $1\frac{1}{4}$  hr., a 3-in. dia. steel ball was driven through the hole. In this case the test-pieces contained copper 0.26% and 0.09% respectively. The former plate exhibited tears in the surface zones which had undergone the greatest deformation, whilst there were none of these tears in the latter plate.

It was noticed that the copper-bearing steel displayed carbide coalescence in the grain boundaries; the reduced ductility associated with this condition explains the red-shortness which had been observed in these copper-bearing steels above the lower transformation point.

**Aeronautical Applications of Instrument Springs.** J. W. Rockefeller, jun. (Wire and Wire Products, 1942, vol. 17, Mar., pp. 139-141, 166). The author discusses the design of aeronautical instrument springs which are self-compensating for the changes in stiffness



caused by temperature changes in the range of  $-50^{\circ}\text{F.}$  to  $+150^{\circ}\text{F.}$  When a spring is used in conjunction with a Bourdon tube or bellows it has to have a positive temperature coefficient of elastic modulus so as to compensate the negative coefficient of the steel or material of which the Bourdon tube is made. It has been found that at 36% of nickel in an iron-nickel alloy series the thermal characteristic reaches a maximum; this alloy is therefore frequently used for springs in pressure gauges and other aeronautical instruments.

**Stainless Steel Developments in Process Industries.** G. A. Sands. (Chemical and Metallurgical Engineering, 1942, vol. 49, Apr., pp. 88-91). The author reviews the properties of martensitic and ferritic chromium steels and of austenitic chromium-nickel steels, and discusses the development of their applications in the chemical industry with particular reference to nitric-acid plants.

A nitric-acid test well known in the United States for evaluating the corrosion resistance of stainless steel is described. This consists of determining the loss in weight of a prepared specimen of the steel after five successive 48-hr. periods in boiling 65% nitric acid; the loss in weight is converted by a factor into a corrosion rate expressed in inches of penetration per month.

**Austenitic Stainless Steels in Process Industries.** G. A. Sands. (Chemical and Metallurgical Engineering, 1942, vol. 49, May, pp. 132-135). In continuation of his previous paper (*see* preceding abstract) the author deals in some detail with the use in process industries of austenitic chromium-nickel, chromium-manganese, chromium-nickel-columbium-titanium, chromium-nickel-molybdenum and chromium-nickel-molybdenum-cobalt steels, discussing in particular the heat treatment and welding of these steels.

**Iron, Sulphur and Manganese.** F. Oldershaw. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, July 2, pp. 231-232). The author briefly discusses the effects of sulphur and manganese in cast iron, the forms which iron sulphide and manganese sulphide take on solidification of the iron and the appearance of the surface of molten iron in the ladle with melts high and low in manganese.

**Physical Properties of Driven and Undriven Rivets of High-Strength Structural Steels.** (Proceedings of the American Society of Civil Engineers, 1942, vol. 68, May, pp. 751-773). This paper constitutes a progress report of the Committee of the Structural Steel Division on Structural Alloys appointed by the American Society of Civil Engineers. In it the results are presented of a number of behaviour tests and strength tests on rivets made of low-alloy high-tensile steels of various analyses. Suggestions are made for the acceptance testing of any low-alloy steel proposed for use as rivets.

**A Note on the Use of the Electric-Arc Furnace in the Laboratory.** J. Steiner. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1941, vol. 47, Aug., pp. 581-587). The



author developed a simple electric-arc furnace for laboratory use, which is especially suitable for the production of ferro-alloys in quantities of up to about 20 kg. A photograph and a diagram of the furnace are reproduced and its construction is described in detail.

**Ferrous Pipes and Piping Installations for and in Connection with Land Boilers.** (British Standards Institution, No. 806—1942).

## METALLOGRAPHY AND CONSTITUTION

(Continued from p. 124 A)

**Some Photometric Instruments Used in X-Ray Diffraction and Spectrographic Methods of Analysis.** J. W. Ballard, H. I. Oshry and H. H. Schrenk. (United States Bureau of Mines, Apr., 1942, Report of Investigations No. 3638). The authors give detailed descriptions of a recording microphotometer and three non-recording densitometers for measuring lines on X-ray films or spectrographic plates. These instruments are simple in design, can be constructed economically and have a number of features that make them stable and easy to operate.

**X-Ray Investigations of Lattice Distortions.** R. Fricke. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1940, vol. 46, Sept., pp. 491–498). The author gives a detailed review of recent work on the investigation of various types of lattice distortion with the aid of X-rays.

**Examination of Material by X-Rays.** A. Trost. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1940, vol. 46, Sept., pp. 508–512). The author reviews the development of X-ray methods of examining materials, dealing with the most important older discoveries and presenting a summary of the latest developments. Among the latter is the application of the indicator valve for measuring X-ray radiation developed by the Reichs-Röntgenstelle, with which a direct reading of the intensity of the rays passing through a material is obtained from a milliammeter. This instrument is capable of indicating high intensities in 0.1 sec. As the indicator valve has a large measuring surface (not less than 1 sq. cm.), it is not suitable for detecting small defects, which means that the screen and film are essential for detecting cracks and small isolated pores. The indicating-valve method has, however, the advantage of being more sensitive and rapid than the film method, and it gives quantitative indications of defects without requiring any photographic materials; it can be used for making continuous wall-thickness measurements and for detecting corrosion in tubes, cylinders for compressed gas and large pressure vessels. The degree of accuracy for steel in thicknesses of from 0.01 mm. to 30 mm. is about 1% of the thickness in 0.1 sec. indicating time. The method is suitable for testing castings up to about 300 mm. thick for

porosity, but for thicknesses exceeding 100 mm. it is better to use  $\gamma$ -rays from radio-active preparations.

In the examination of lattice structures the indicator-valve method has advantages in many cases, for it indicates the position of very weak interference lines rapidly and with very great accuracy.

**Radiography as a Foundry Tool.** P. McCaffery. (Iron Age, 1942, vol. 149, May 14, pp. 45-48). The author describes some examples of the application of X-ray technique in the steel foundry to discover defects in castings and to check the adequacy of repairs by welding.

**Signs for Heterogeneous Equilibria.** ("Metallographic Letters"). H. Hanemann. (Aluminium, 1941, vol. 23, Nov., pp. 517-518; Zeitschrift für Metallkunde, 1941, vol. 33, Nov., pp. 374-375). The author suggests that standardised symbols should be adopted to represent words used in the descriptions of heterogeneous equilibria and gives examples of suitable symbols or signs for such expressions as "binary eutectic," "ternary eutectic" and "binary monotectic structure."

**Intermetallic Phases with Partial Heteropolar Linking.** U. Dehlinger. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1940, vol. 46, Nov., pp. 627-634). In a study of the linking in intermetallic phases the author attempts to classify alloys in empirical groups such that the linkings of the components of each alloy of one group obey the same or similar laws, and, as a test for the validity of his classification, he examines whether, under the assumed conditions of linking, the experimentally determined structure and no other must result, and whether it is stable. He shows that even in intermetallic compounds of stoichiometric composition not all atoms are ionised, but some remain irregularly distributed and able to furnish outer electrons for metallic linking. This irregular distribution increases the entropy and therefore the thermodynamic stability at high temperatures. This accounts for the striking fact that many intermetallic compounds have a wider range of composition at high temperatures.

**The Crystal Structures of Fe, FeO and Fe<sub>3</sub>O<sub>4</sub> and their Interrelations.** H. J. Goldschmidt. (Iron and Steel Institute, 1942, this Journal, Section I.). A simple relation is shown to exist between the lattice dimensions of the three phases of the iron-oxygen system:  $\alpha$ -iron (Fe), wüstite (FeO) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The close connection between the three structures, which are all cubic, explains why a comparatively easy transition from Fe to FeO, from Fe to Fe<sub>3</sub>O<sub>4</sub> and from FeO to Fe<sub>3</sub>O<sub>4</sub> is possible under practical oxidising conditions implying limited access of oxygen. While the transition Fe  $\rightarrow$  FeO is considered as a true oxidation, the change FeO  $\rightarrow$  Fe<sub>3</sub>O<sub>4</sub> is not, because the number of oxygen ions per crystal volume remains constant, only iron being lost. The wüstite range of solid solutions is discussed from the same aspect; the omission of ferrous Fe<sup>++</sup> ions from lattice points under

partial replacement by ferric  $\text{Fe}^{+++}$  ions is preparatory to the change-over to the  $\text{Fe}_3\text{O}_4$  structure. The linear decrease of lattice spacing of wüstite with increasing oxygen content, as found by Jette and Foote, is utilised. It is observed that the lattice parameter of the  $\text{Fe}_3\text{O}_4$  unit cell is in direct linear continuation of the same decrease. The ionic replacements within the lattice during this process are considered numerically in some detail; they finally lead to a distribution of ions agreeing with the known spinel structure.

The structure of  $\gamma$ -iron is intimately connected with that of  $\text{FeO}$ , a fact which is corroborated by comparing the atomic volumes of all the phases concerned. It is suggested by this comparison that similar relations exist between  $\alpha$ -Fe and  $\text{Fe}_3\text{O}_4$  on the one hand and  $\gamma$ -Fe and  $\text{FeO}$  on the other, each pair of phases being thus fundamentally associated, and that the  $\gamma$ - $\alpha$  change at  $906^\circ \text{C.}$  is coupled with the decomposition of  $\text{FeO}$  at  $750^\circ \text{C.}$ :  $[\text{4FeO} \longrightarrow \text{Fe} + \text{Fe}_3\text{O}_4]$ .

The results of some X-ray tests on layers of scales formed on pure iron are included mainly to illustrate two points: (1) The decrease of the wüstite lattice constants with decreasing iron content. (2) The effect on the structure of the scale of exposing either  $\alpha$ -Fe or  $\gamma$ -Fe to oxidising conditions.

The latter preliminary experiments revealed the innermost layer of scale to be pure wüstite if formed at, and quenched from, temperatures above  $A_3$ , and wüstite plus magnetite below  $A_3$ , the proportion of magnetite increasing with decreasing temperature.

The facts discussed have a bearing on the problem of the corrosion resistance of steel.

## CORROSION OF IRON AND STEEL

(Continued from pp. 124 A–128 A)

### Salt Spray Evaluation of Oiled Black Oxide Coatings on Steel.

A. K. Graham. (Metal Finishing, 1942, vol. 40, June, pp. 254–255). The author makes recommendations for the standardising of salt-spray tests on oiled black-oxide coatings on steel.

**Auto-Nitrification of Steel as It Scales.** G. H. Enzian, H. F. Beeghly and P. P. Tarasov. (Metal Progress, 1942, vol. 41, Apr., pp. 522–526). The authors discuss the results of an analytical and metallographic investigation of some corroded nails recovered from the wreckage after a volcanic eruption at St. Pierre, Martinique (see p. 80 A). With regard to the abnormally high nitrogen content of the corroded nails, it is probable that nitrogen will not readily diffuse through an appreciable continuous layer of scale, and therefore any of this gas either dissolved or combined with iron will remain in the metal. Since there is a loss of iron and other elements at the surface with little loss of nitrogen, the relative nitrogen

content of the steel near the surface is increased and, in effect, a nitrogen concentration gradient is created with decreasing values towards the core. Some tests with a  $\frac{5}{8}$ -in. dia. steel bar heated in an open furnace confirmed this theory.

**The Destruction of Material by Cavitation in a Vibration Testing Apparatus.** T. Rutenbeck. (*Zeitschrift für Metallkunde*, 1941, vol. 33, Apr., pp. 145-152). The different methods of causing cavitation erosion are discussed and compared. This form of erosion takes place under a wide variety of hydrodynamic conditions, but the fact of major importance is that a vapour phase occurs. Cavitation erosion testing by a vibratory method is dealt with at length and a new type of testing apparatus is described and compared with that of Kerr (*see Journ. I. and S.I.*, 1939, No. I., p. 247 A). Oscillations of very high amplitude can be produced with the new apparatus. Photographs of bubbles and the loss of weight at different temperatures, at different vapour pressures and under different external pressures is studied. Photomicrographs of different stages of cavitation erosion reveal that primary and secondary corrosion takes place, the former in only 0.5 sec. As a rule the damage is of three types: plastic deformation, melting and erosion pits. The mechanism of the primary corrosion is associated with the occurrence of local temperature peaks which account for the high velocity of the chemical reactions and for the marked plastic deformation even to the extent of the melting of minute particles; in the secondary stage the surface which has been worked in this way is subjected to fatigue or corrosion-fatigue to such an extent that considerable loss of weight takes place.

**Droplet Impact Investigations for Determining Resistance to Cavitation.** M. von Schwarz. (*Zeitschrift für Metallkunde*, 1942, vol. 33, June, pp. 237-244). The author describes an investigation of the mechanism of cavitation which he carried out in collaboration with Mantel and Steiner using an apparatus in which specimens of highly polished brass and stainless steel mounted on a two-armed carrier were revolved at high speed so as to cut through a jet of water. The tests were made at different speeds and temperatures, and the loss in weight was determined after various periods of attack. Photographs of the pitted surfaces are reproduced. The following conclusions were arrived at: (1) Cavitation is caused mainly by the mechanical action of the water during which the extremely rapid collapse of bubbles gives rise to blows at pressures of up to 30,000 kg. per sq. cm. (2) The velocity at which the blades cut the water is the factor which has most effect on the rate of pitting. (3) The action of the water referred to in (1) first cold-works the metal surface and the cavitation effect begins after this effect has disappeared. (4) Up to a certain critical point the cold-work promotes the resistance to cavitation, above this point it is detrimental. (5) The grain size, hardness and homogeneity of the



metal are also of importance, but do not have so much effect as the cold-work.

**Intercrystalline Cracking of Boiler Steel and Its Prevention.** W. C. Schroeder and A. A. Berk. (United States Bureau of Mines, 1941, Bulletin No. 443). The authors report on an extensive investigation carried out by the Joint Research Committee on Boiler Feed-Water Studies in co-operation with the Bureau of Mines. A detailed study of how the cracks occur was first made, and from the deductions drawn a test equipment for measuring the embrittling effect of a boiler water was developed, together with methods of evaluating feed-water treatments. If a solution that produces general over-all corrosion is modified and a chemical added that tends to protect the crystal faces of the boiler material, the general activity at these surfaces may be reduced and corrosion focused on the boundary atoms; this is the part that silica is believed to play in accelerating embrittlement cracking in sodium hydroxide solutions. As all of these processes are delicately balanced, the silica does not necessarily have the same effect throughout the temperature range of boiler operation. It may produce a coating that will encourage selective penetration at relatively high temperatures, although it has no effect at low temperatures. At low temperatures too, silica may cover the entire surface and actually retard action at the boundaries. The selective-corrosion theory provides the only explanation as yet put forward that reasonably correlates the intricate mass of experimental facts repeatedly demonstrated to be involved in this cracking process.

The equipment described for testing the effect of boiler-waters can be used not only in the laboratory, but it can also be attached directly to a stationary or locomotive boiler. When on a boiler, a portion of the water continually passes through the unit to ensure duplication of operating conditions and to avoid all errors in sampling. This detector is now used to classify boiler-waters as embrittling or non-embrittling. Tests with the detector have shown that the addition of sulphate or other inorganic salts in high concentration to a water that is non-embrittling owing to the presence of organic matter may be undesirable. Treatment of locomotive boiler-waters with waste sulphite liquor has in most cases eliminated the cracking of specimens in the detectors attached to locomotives. Sodium nitrate has been found very effective in preventing intercrystalline cracks in laboratory detector tests at 200 or 300 lb. per sq. in. For boilers using distilled make-up water, especially at pressures above 400 or 500 lb. per sq. in., preliminary test results indicate that embrittlement cracking can be reduced or eliminated by using tri-sodium phosphate instead of sodium hydroxide or sodium carbonate to maintain the pH value.

**The Use of Statistical Control in Corrosion and Contact Resistance Studies.** W. E. Campbell. (Electrochemical Society, Apr., 1942, Preprint No. 81-26). It is pointed out that valid predictions from

experimental data cannot be made unless the data are in statistical control; this fact is a serious handicap in studies of certain corrosion processes where the magnitude of the effect being studied is of the same order as that of the range of fluctuation. The author discusses this problem, using as an example the study of data on the electrical resistance of a contact between a platinum-iridium alloy sphere 0.2 in. in dia. and a flat plate of the metal the contact resistance of which is to be determined. Statistical criteria are described which can be used to aid in detecting and eliminating the causes of lack of statistical control.

## ANALYSIS

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(Continued from pp. 80 A-83 A)

**Electrographic Analysis.** E. A. Arnold. (Steel, 1942, vol. 110, Apr. 20, pp. 74-76). After outlining the principles underlying the electrographic method of analysis, which is a special form of spot test, the author briefly describes its application to the qualitative and quantitative determination of alloy components in steel, especially nickel, and discusses the possibility of detecting pin holes in metallic coatings with the aid of the electrographic method. In conclusion he gives a survey of the literature which has a bearing on the subject.

**Rapid Steel Analysis.** A. C. Titus. (Iron Age, 1942, vol. 149, Apr. 9, pp. 56-58). The author describes how rapid analyses are made at the iron and steel foundry of the General Electric Co., Schenectady, to determine the carbon, molybdenum and manganese.

**Steel Analyses by Drop Reactions.** G. Thanheiser and Maria Waterkamp. (Iron and Steel Institute, 1942, Translation Series, No. 95). An English translation is presented of a paper which appeared in Archiv für das Eisenhüttenwesen, 1941, vol. 15, Sept., pp. 129-144. In this procedures are described for detecting the presence of a large number of alloying elements in steel by means of drop reactions which are not harmful to the surface of the specimen. (See Journ. I. and S.I., 1942, No. I., p. 253 A).

**Electrolytic Determination of Iron.** W. H. Armistead. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Mar., pp. 207-209). The author suggests a more rapid and accurate way of carrying out Moore's method of determining iron by electrodeposition from complex ferric-phosphate/ammonium-carbonate solutions. The modified method may be applied to the analysis of low-manganese iron ores without removal of hydrochloric acid. Small amounts of nickel, molybdenum and cobalt are quantitatively co-deposited with large amounts of iron. Tungsten

as well as nitrates and oxidising agents interfere with the determination, whereas large amounts of phosphate, chloride and sulphate may be present.

**Determination of Copper and Nickel in Steels.** L. Silverman, W. Goodman and D. Walter. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Mar., pp. 236-237). The authors developed a method for the determination of copper and nickel in steels, in which copper is electrodeposited at room temperature, without stirring, from solutions which, after the addition of ammonia, have been acidified with sulphuric and phosphoric acid. After the deposition of copper, nickel is determined by titration with cyanide, no preliminary separation with dimethylglyoxime being necessary.

**Colorimetric Determination of Phosphorus in Iron Ore.** E. J. Center and H. H. Willard. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Apr. 15, pp. 287-288). The authors suggest a slight modification to the procedure which they previously described for the determination of phosphorus in iron ore. (See Journ. I. and S. I., 1941, No. II., p. 58 A.)

**The Polarograph—Its Limitations and Advantages.** (Sheet Metal Industries, 1942, vol. 16, May, pp. 619-622). A detailed description is given of the polarograph, an instrument for the analysis of aqueous solutions by the measurement of current/voltage relationships during electrolysis of the solution. Small quantities of solution only are required, and the method may be regarded in many respects as intermediate between the chemical and spectrographic processes of analysis. Most metals and a large number of inorganic and organic radicles, as well as other organic substances, can be detected, and many of them determined quantitatively.

**Determining the Fusain Content of Illinois Coals.** B. C. Parks, G. W. Land and O. W. Rees. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Apr. 15, pp. 303-305). The authors compare the results obtained when determining the fusain content of Illinois coals by the A.S.T.M. standard procedure and by the petrographic (microscopic-count) method, and arrive at the conclusion that the latter method is to be preferred.

**Determination of Ash in Coals Unusually High in Calcite and Pyrite.** O. W. Rees and W. A. Selvig. (Industrial and Engineering Chemistry, Analytical Edition, 1942, vol. 14, Mar., pp. 209-212). The authors present a report of co-operative work done by the Analytical Laboratory of the Illinois State Geological Survey and the Pittsburgh Laboratory of the United States Bureau of Mines for the purpose of studying the determination of ash in coals containing unusually large amounts of calcite and pyrites, the analysis of which by the standard A.S.T.M. procedure offers difficulty because various amounts of sulphur are retained in the ash in the form of calcium sulphate. Seven modifications of the standard procedure were tried out and the results obtained are critically reviewed.

**British Standard Methods for the Sampling of Coal and Coke.**  
(British Standards Institution, No. 1017—1942).

**British Standard Methods for the Analysis and Testing of Coal and Coke.** (British Standards Institution, No. 1016—1942).

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## REFRACTORY MATERIALS

(Continued from pp. 131 A-132 A)

**The Heat Treatment of Refractory Materials.** N. W. Taylor and S. Zerfoss. (Heat Treating and Forging, 1942, vol. 28, May, pp. 244-248). The authors review the literature on methods of investigating the properties of refractory materials and non-metallic minerals.

**Survey of Literature on Slag Tests for Refractory Materials.** T. L. Hurst and E. B. Read. (Journal of the American Ceramic Society, 1942, vol. 25, July, pp. 283-294). The authors present a survey of the literature on slag tests for refractory materials for the period 1932-1940, together with a classified index to methods of testing and means for evaluating slag attack. The bibliography contains 166 references.

**An Investigation on the Manufacture of Carbon Blocks for Blast-Furnace Hearths.** G. R. Rigby, H. Booth and A. T. Green. (British Refractories Research Association: Transactions of the British Ceramic Society, 1942, vol. 41, May, pp. 144-147). The literature relating to the manufacture and use of carbon blocks in blast-furnace hearths is reviewed. The preparation of briquettes from foundry coke and gasworks pitch is described, and the feasibility of dry-press or tamping methods of manufacture demonstrated. The properties of the specimens prepared in the laboratory compared favourably with those of a German commercial product.

**Refractories Service Conditions in the Blast Furnace.** H. M. Kraner. (Journal of the American Ceramic Society, 1942, vol. 25, July, pp. 311-320). The author examines the problem of the wear of blast-furnace linings by surveying the literature and presenting information gained by chemical and mineralogical studies of refractory bricks removed from linings at the end of a campaign. The combined action of alkali attack and of disintegration of bricks due to the deposition of carbon operates approximately as follows: The zone of severe disintegration due to carbon develops at 450-550° C., and is wider at the top of the furnace than at the mantle; it is also near the inner face at the top and closer to the shell at the mantle. As the alkali reaction removes the brick face, the temperature gradient between the working face and shell changes, and the disintegrating zone advances towards the shell. Alkali attack and the advancing disintegrating action therefore proceed simultaneously. Comprehensive tables of analyses of used bricks from various parts of the blast-furnace are presented, together with diagrams showing the wear and slag encrustations at different levels. A classified bibliography with 75 references is appended.

**Acid Open-Hearth Refractories.** J. H. Chesters. (Iron Age, 1942, vol. 149, May 28, pp. 46-51; June 4, pp. 65-70). The author

discusses the materials used, the life and causes of failures and possible line of improvement in the refractories used for the various parts of acid open-hearth furnaces. The main chance of improving the roof life lies in the application of recording pyrometers, and an attempt is being made to devise special gear to make the removal of thermocouples in back walls easier, but this presents serious difficulties. If finely ground siliceous material, namely, silica flour, were incorporated in the sand used for the hearths, so that the interstices between the sand grains were filled with material of similar refractoriness, an improved life would be obtained, and some preliminary laboratory and works tests have shown that such a procedure is practicable and that it results in a definite improvement on existing practice. The ports, walls, gas and air uptakes and checkers are also considered.

## FUEL

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(Continued from p. 132 A)

**Fuel Saving in the Iron and Steel Industry with Special Reference to Sheffield Practice.** (Iron and Steel Industrial Research Council, British Iron and Steel Federation, June, 1942). This is a report prepared at the request of the Mines Department, on the possibilities of effecting improvements in fuel consumption in iron and steel practice. After surveying the fuels used, practical methods by which fuel can be saved in boiler practice are dealt with under the following headings: (1) The suitability of coals for steam-raising; (2) general hints on boiler-house control for superintendents and firemen; (3) steam utilisation; and (4) steam measurement. In the latter part of the Report economies for re-heating and heat-treatment furnaces, the use of mechanical stokers, adjustment of gas burners and gas-producer practice are considered.

**An Organisation of Fuel Department Personnel and Practice.** T. J. McLoughlin. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 61-66). The author presents a chart showing fuel production and consumption at a fully integrated steel plant working at full capacity and producing 5,000,000 tons of ingots per year. He discusses the organisation and responsibilities of the staff of the fuel department for such a plant as well as the requirements of a suitable standard cost system.

**Stoker Application for Combination Firing of Boilers.** O. de Lorenzi. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 74-78). The author reviews developments in the design of boilers for steel-works use which are fired with a combination of blast-furnace gas and coke breeze. The type favoured by the author has a large upper combustion chamber with the gas burner well above the mechanical stoker.



**Standard Methods of Measuring Extent of Atmospheric Pollution.** C. E. Brown and H. H. Schrenk. (United States Bureau of Mines, May 1942, Information Circular No. 7210). The authors review methods of determining the concentration of gases, liquids and solids contaminating industrial atmospheres.

**Studies on Coking Pressures.** W. Fuchs and A. G. Sandhoff. (Fuel in Science and Practice, 1942, vol. 21, July-Aug., pp. 70-73). The authors report the results of laboratory investigations of the influence of certain variables on the swelling pressure of coking coals. The following conclusions were arrived at : (1) In the small experimental ovens the pressure decreases with increasing width of oven ; (2) the pressure decreases with increasing percentages of volatile matter in the coal ; (3) weathering the coal materially diminishes the pressure ; (4) increasing the moisture content of the coal to about 5% considerably reduces the pressure ; and (5) the addition of various ammonium and sodium salt solutions to the coal does not reduce the pressure to any material extent.

**The Caking and Swelling Power of Coal.** R. A. Mott. (Fuel in Science and Practice, 1942, vol. 21, May-June, pp. 51-61 ; July-Aug., pp. 80-88). The author shows how the results of different forms of swelling tests for coking coals can be related to the coal analyses, and suggests a basis for terms which would avoid the confusion which at present exists. His conclusions are as follows : (1) All swelling tests show a general relationship between swelling and the composition of bright coal, the swelling increasing with the carbon content and also with the hydrogen content of the coal ; durain is non-swelling in all tests. (2) The Gray-King assay fails to reveal the swelling power of coals of low rank because of the freedom for gas escape from the large exposed surface of the coal. (3) The Sheffield University laboratory coking test can be used to measure the swelling power of strongly swelling coals, but fails, at the slow rate of heating previously used, to reveal the swelling power of coals of very low rank. (4) The Lessing volatile-matter test, whilst it is more generally suitable as a measure of swelling than the crucible volatile-matter test, fails to assess correctly the swelling power of moderately swelling coals owing to too rapid a rate of heating. (5) The British Standard crucible swelling test is the simplest of all the swelling tests considered, yet it reveals more completely than any other test the swelling properties of coal over almost the whole range of agglomerating coals. (6) The swelling power of lump bright coal can be represented most satisfactorily by the percentage of swelling in, and by the isodemes (lines of equal swelling) of, the British Standard crucible swelling test. (7) The swelling power of any coal, being affected in all methods of testing by the hydrogen content, as well as by the carbon content, is more directly proportional to the calorific value of the pure coal than to its carbon content. (8) No single swelling test should be relied upon to assess the caking or swelling properties of coal, for all are subject to certain errors ; if

the swelling property of a coal, as revealed by tests, conforms to that expected from its analysis, confidence can be placed in the data.

The author makes the following recommendations on nomenclature for the laboratory testing of coals: (a) The terms "non-agglomerating" and "agglomerating" to be used for coals which, in powder form, give, in effect, a non-coherent coke button or a coherent coke button in the crucible test; (b) the term "agglutinating value" should be retained to describe the sand test; (c) the terms "weakly caking" and "strongly caking" should be replaced by "weakly swelling" and "strongly swelling," and the term "caking" should not be used; and (d) the term "coking coal" should be reserved for a coal which will yield, in a coke-oven, a commercial coke.

**Expansion of Coal during Coking.** J. T. McCartney and J. D. Davis. (United States Bureau of Mines, May, 1942, Report of Investigations No. 3644). The authors report on an investigation of the expanding properties of "borderline" coals, *i.e.*, coals the swelling power of which might be dangerous to the coke-oven walls. Two types of test-oven were used—a vertical slot oven having one movable side wall, and a sole-heated oven in which either pressure developed at constant volume, or expansion at constant pressure, could be determined. Based on the number of coals tested, the following conclusions appeared to be justified: (1) Borderline coals, when coked from both sides show peak pressures at constant volume near the end of the coking period that are very much higher than any obtained with heating from one side only; (2) thin charges of less than 10 in. in the vertical slot oven gave higher peak pressures than charges 10 in. and 13 in. thick; (3) with the single blend tested, peak pressures in the vertical oven did not vary much with different wall-heating programmes; (4) the gas pressure at the centre of incompletely coked charges of the vertical slot-oven became appreciable only at or near the time of development of peak pressure; and (5), fair correlation between expansion and plastic properties was evident, the results obtained by the Gieseler plastometer apparently being the best upon which to base this correlation.

**The Utilisation of Low-Grade Fuels in Gas Producers.** M. W. Thring. (British Coal Utilisation Research Association: Journal of the Society of Glass Technology, 1942, vol. 26, June, pp. 145–154). Some preliminary suggestions for reducing the disadvantages of using low-grade fuels in gas producers are put forward. A study of the fundamentals of gasification has brought to light a number of new possibilities, of which the most important is that, by reducing the voids in that part of the bed first reached by the air, it is possible to get good producer gas and low temperatures simultaneously. It is suggested that the addition of coke to caking fuels may enable them to be gasified at a rating more closely approaching the normal. The use of a feed-cylinder is suggested to reduce carry-over of dust when gasifying dusty or friable fuels, whilst fuels of wide size-ratio

are best gasified in producers designed to segregate the large particles away from the walls. Clinkering of fuels with low ash-fusion temperature may be reduced by the addition of sand. Apart from these suggestions it is concluded that almost any fuel can be gasified with a corresponding reduction in throughput and increase in labour.

## PRODUCTION OF IRON

(Continued from pp. 133 A-134 A)

**Recent Installations for Conditioning the Air Used in Blast Furnaces.** E. K. Miller. (American Iron and Steel Institute: Industrial Heating, 1942, vol. 9, Mar., pp. 332-334). The author discusses some of the advantages which have resulted from the installation of dehumidifying plant at the blast-furnaces of the Jones and Laughlin Steel Corporation. The equipment is adjusted to reduce the moisture content of the blast to 3 grains per cu. ft. It has not been in operation very long, but a 5% increase in pig-iron production and 3% less coke consumption have already been noted.

**The Relations between Oxygen Pressure, Temperature and Composition in the System  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$ .** N. G. Schmahl. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1941, vol. 47, Dec., pp. 821-835). After a detailed review of the literature on the hematite-magnetite system, the author reports on his study of the system by isothermal decomposition at various temperatures between 1290° and 1410° C. On the basis of his results he suggests some modifications of White's  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  phase diagram (see The Iron and Steel Institute, Carnegie Scholarship Memoirs, 1938, vol. 27, pp. 1-75), especially with regard to the phase boundaries in the solid state. In order to demonstrate the effect of the oxygen pressure on the equilibrium in the system, the author includes two isobars in his diagram, viz., those for oxygen pressures of 159 and 760 mm. of mercury.

**Concentration of Blast-Furnace Flue Dusts.** S. M. Shelton and F. D. Lamb. (Iron Age, 1942, vol. 149, June 11, pp. 54-59). The authors report on laboratory investigations of magnetic, gravitation and flotation methods of concentrating blast-furnace flue dust. The results of many tests are given in tables, and the conclusions drawn were: (a) The magnetic concentration of flue dust is a practical and commercial proposition; tests on unroasted dust yielded concentrates assaying 65.5% of iron with a recovery of 65.8% of total iron. After reduction roasting, magnetic concentrates were made assaying 65.9% of iron, representing an iron recovery of 95.8%. (b) Gravity concentration tests were not as successful as magnetic separation tests because of the extremely fine particle size of a large portion of the iron in the flue dust. (c) Flotation tests were not sufficiently successful to justify this process as a means of beneficia-

ting the flue dust. Concentrations assaying 56.3% of iron were obtained by flotation of the coke particles as a means of concentrating the iron; the recovery amounted to 92.8% of the total iron.

**British Standard Specification for Air-Cooled Blast-Furnace Slag Coarse Aggregate.** (British Standard Institution, 1942, No. 1047). This Specification refers to the supply of air-cooled blast-furnace slags up to  $1\frac{1}{2}$  in. nominal maximum size for use as coarse aggregates in concrete for normal structural purposes, including roads.

## FOUNDRY PRACTICE

(Continued from pp. 134 A–137 A)

**Cupolas and Materials.** D. J. Reese. (American Foundrymen's Association: Canadian Metals and Metallurgical Industries, 1942, vol. 5, June, pp. 160–163). The author makes recommendations for improving the efficiency of cupola operation.

**The Substituting of High-Duty Grey Iron for Steel Castings.** J. Blakiston. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, July 9, pp. 241–246, 251; July 16, pp. 263–269). In the first part of this paper the author briefly describes and illustrates some examples of the use of high-duty grey cast iron in place of steel; these are proved cases, not experiments, and they include a boring bar 45 ft. long, 16 in. in dia.; a large boring lathe-head; a milling-machine spindle and spindle-neck; parts of a heavy planing machine; gear wheels; pump bodies and other pump parts. Some simple and convincing tests demonstrating the strength of high-duty cast iron are described. In the second part details of two cupolas, one 33 in. in dia., the other 20 in. in dia., the method of charging, the melting losses and the inoculation with ferro-silicon to produce high-duty iron are given.

**Chilled Wheels for Streetcars.** W. F. Chubb. (Metallurgia, 1942, vol. 26, June, pp. 49–52; July, pp. 83–84). The author describes briefly the method adopted in American foundries for producing chill-cast wheels for trams, and then gives an account of research work undertaken in attempts to improve the quality of the product. It was found that chill-cast wheels containing about 1.75% of nickel and 0.5% of chromium are in every way superior to unalloyed irons, but it is necessary to increase the silicon from 0.60% to 1.00% to control the depth of chill and to prevent a sharp transition zone from forming between the chilled and mottled sections.

**Some Effects of Hydrogen on the Time of Malleableization.** C. H. Lorig and M. L. Samuels. (American Foundrymen's Association, Apr., 1942, Preprint No. 42–7). The authors describe experiments the object of which was to determine the influence of hydrogen in cast iron on the time required for malleablising. A number of



melts were prepared of iron of the short-time malleablising type by : (a) Melting in the conventional manner, (b) using stock which had previously been held at suitable temperatures to drive off any dissolved and occluded hydrogen, and (c) melting in a crucible and bubbling hydrogen through the melt before casting. Small specimens were given a heat treatment at temperatures in the 300–1300° F. range with holding times varying between 30 min. and 8 hr. before malleablising. This treatment was found to cause a considerable refinement of the temper carbon structure and to increase considerably the rate of malleablising in both the first and second stages. The melts saturated with hydrogen were even more responsive to the preheating treatment than those produced in the usual manner. The authors conclude that faster malleablising may be explained by the presence of a greater number of temper carbon nodules in the pretreated irons than in those malleablised in the as-cast condition. The temper carbon nodules originating from nuclei were smaller in the specimens which had had the low-temperature pretreatment. The formation of nuclei is apparently associated with the escape of hydrogen, but the exact mechanism involved is still unknown.

**Moulded Gear Wheels.** J. Timbrell. (Foundry Trade Journal, 1942, vol. 67, July 30, pp. 312–313). A brief account is given with several drawings of how to prepare a mould with a combined stripping plate and cover core for casting iron gear wheels.

**Diagnosing a Cylinder Cover Casting. I. General Details Examined.** A. F. Hammond. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, July 23, pp. 287–288). The author discusses the following items contributing to the manufacture of a cast-iron cylinder cover for a hydrogen compressor : (a) the drawing ; (b) design ; (c) specification and general requirements as to soundness ; and (d) conditions under which the casting will be used.

**Diagnosing a Cylinder Cover Casting. II. Machine Moulding.** L. E. Slater. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Aug. 13, pp. 351–352). The author outlines how the planning and pattern equipment department of his foundry would have been instructed to prepare the patterns for producing, by machine moulding, the casting referred to in the preceding abstract.

**Diagnosing a Cylinder Cover Casting. III. Production in Meehanite Metal.** J. King. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Aug. 20. pp. 371–372). The author describes how the cylinder cover referred to in the two preceding abstracts was cast in Meehanite. Experiments were made with two core mixtures, one of silica sand with an oil-binder, and the other containing an addition of 12% of cast-iron borings, which were first passed through an  $\frac{1}{8}$ -in. mesh sieve. The more rapid cooling with the latter mixture induced a much higher hardness in the casting. The runners and risers were arranged to get the hottest metal at the uppermost part of the casting, thus facilitating progressive solidification.

## PRODUCTION OF STEEL

(Continued from pp. 137 A-139 A)

**Atlantic Steel Company.** T. J. Ess. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 45-52). A detailed illustrated description is given of the steel plant and rolling mills and the Atlanta Works of the Atlantic Steel Co. The plant comprises three open-hearth producer-gas-fired furnaces with hearths 31 ft.  $\times$  13 ft. 6 in., blooming, billet and bar mills, hoop mills and a wire mill.

**Design, Operation and Construction of a Bessemer Converting Mill.** D. R. Loughrey. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 28-37). The author describes the layout and components of a Bessemer plant, dealing in turn with the mixer, converters, lining shop, control pulpit, blowing plant, cranes, casting pits and ladles. He also gives a detailed account of the changes in the appearance of the flame as the blowing proceeds—an account which is illustrated with twelve photographs in colour.

**Recovery and Preparation of Steel Scrap.** F. E. Ullman. (Steel, 1942, vol. 110, June 29, pp. 75-78; vol. 111, July 6, pp. 97-98, 122). The author describes the equipment and process for recovering steel and lumps of steel-bearing slag from old heaps of steel-furnace slag, as well as equipment for recovering it from slag produced as the steelmaking proceeds. In the latter case, slag and refuse, usually in thimbles and side-tipping wagons respectively, are brought under an overhead crane runway and dumped into a hot slag pit. This material is then broken up with a drop-ball in this pit and fed into a separator. The cost of recovery and preparation of steel scrap from the currently produced slag and refuse depends entirely on the character of the materials being handled. The average loss of steel in American practice into the slag and refuse is from 3% to 6% of the ingot production of the furnace; 95% of this loss can be recovered by the methods described. The cost of recovery varies widely from plant to plant.

**Considerations Governing Use of Scrap and Pig in Open-Hearth Charge.** C. D. King. (American Iron and Steel Institute: Industrial Heating, 1942, vol. 9, Mar., pp. 343-344, 365). The author discusses the factors which, in American steelmaking practice, determine the proportions of pig iron and steel charged in the steel furnaces. These factors are: (1) The relative availability of scrap and pig iron; (2) the prices of scrap and pig iron; (3) the handling facilities for scrap and molten pig iron which affect the rate of ingot production; and (4) special requirements for the steel produced.

**Conservation of Alloys in the Open-Hearth.** W. J. Reagan. (Metals and Alloys, 1942, vol. 15, May, pp. 741-744). The author discusses methods of reducing the amount of alloying elements found in carbon steels in the manufacture of which none of the elements

was intentionally added. The source of these elements is usually the scrap, and it is suggested that scrap-dealers and steelmakers should pool their information on types of scrap. Examples are quoted which show how the cause of poor-quality steel was traced to contamination with antimony from scrap die-castings and from enamelled ware. As to the detrimental effect of tin, this depends on the carbon content of the steel; with 0.60% of carbon 0.03–0.08% of tin has been found to give trouble, but with only 0.08% of carbon as much as 0.20% of tin may not have any bad effect. The residual manganese in steel can be reduced by controlling the slag and the bath temperature; for a given manganese content of the charge increasing the temperature and lowering the FeO in the slag raises the manganese content of the finished steel.

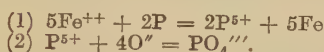
**Desulphurization in the Open-Hearth. Parts I. and II.** F. W. Scott and T. L. Joseph. (Metals and Alloys, 1942, vol. 15, May, pp. 745–750; June, pp. 976–978). In this paper an account is given of the authors' research on the effect of the silica, lime and iron oxide in open-hearth slags on the distribution of the sulphur between the slag and the metal. The rotating furnace previously described (*see* p. 104 A) was used. Much of the information in this paper was given in an earlier one entitled "The Effect of Manganese on the Desulphurizing Power of Calcium Silicates" (*see* p. 138 A), but the present paper also deals with the effect of iron oxide. Iron oxide has a greater effect than any other factor upon the desulphurising power of a basic slag. The sulphur distribution coefficient (*see* p. 138 A) is increased more than 200 times when the iron oxide is reduced by saturating the steel with carbon. When the lime-silica ratio exceeds unity, substantially all the FeO in the slag appears to be free, and is therefore active in controlling the FeO in the metal and the desulphurising power of the slag. The value of the sulphur distribution coefficient shows a slight increase with an increase in temperature. There is evidence that the desulphurising reaction is endothermic; it is promoted by increasing the temperature.

**Observations in the Making and Use of Sulphite-Treated Steels.** E. L. Ramsey and L. G. Graper. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1476: Metals Technology, 1942, vol. 9, Apr.). The authors survey experiments made with regard to the manufacture and properties of steel to which sulphur is added by treatment with sodium sulphite. The sulphite should be added to the ladle last. The recovery of the sulphur is fairly constant at 65–70%. The practice has been to use sodium sulphite when up to 0.050% of sulphur is wanted in the steel, and sodium bisulphite when 0.050–0.090% of sulphur is required. Better sulphur distribution is obtained by the sulphite treatment than by adding stick sulphur, and the steel will roll just as well after the former treatment as when no sulphur is added. The sodium oxide which forms helps to remove inclusions into the slag. An improvement in machining speeds, tool life and surface finish is obtained by

adding sulphur in the form of sodium sulphite to the required amount.

**Manufacture of Bullet-Proof Steel.** A. G. Arend. (Electrician, 1942, vol. 129, July 31, pp. 119-121). The author describes how manganese-vanadium bullet-proof steel was made in electric furnaces in 1918, and discusses some improvements in electric-furnace design and methods of wiring which have taken place since then.

**The Effect of Foreign Ions on the Equilibria between Steel and Molten Slags.** P. Herasymenko. (Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 1941, vol. 47, Aug., pp. 588-594). In the introductory part of his paper the author discusses the general basis of the equilibria between slags and molten steel assuming the complete electrolytic dissociation of molten slags. He points out that the rules for simple electrochemical equilibria between metals and molten halides are applicable also to equilibria between steel and molten slags, especially with regard to the effect of the composition and ion size. He then reports on his study of the phosphorus and manganese equilibria in basic open-hearth slags, which involved the examination of numerous samples taken during the boil. He represents a slightly modified version of his theory on manganese equilibria published in an earlier paper (*see* Journ. I. and S.I., 1940, No I., pp. 279 A), the main difference being that the effect on the equilibrium not only of anions present but also of cations is taken into account. He points out that the phosphorus equilibrium is governed by the following two reactions, both of which are greatly affected by the  $\text{Ca}^{++}$  ions and  $\text{O}''$  ions present :



The phosphorus reaction can be represented in a simple way by the semi-empirical equilibrium constant :

$$k_{\text{P}}^{\text{Fe}} = \frac{c\text{P}(\text{Fe}^{++})^{5/2}}{(\text{PO}_4''')}^2$$

This equilibrium constant is not affected by the  $\text{O}''$ -ion content but decreases with increasing  $\text{Ca}^{++}$ -ion content.

**The Formation of Hair-Line Cracks.—Part I.** J. H. Andrew, A. K. Bose, G. A. Geach and H. Lee. (Iron and Steel Institute, 1942, this Journal, Section I.). The work of Musatti and Reggiori has been confirmed, showing that the soaking of alloy steels in hydrogen at  $1200^\circ \text{C}$ . followed by rapid cooling through the  $\text{Ar}_1$  point results in the formation of internal defects similar to hair-line cracks. The cracks were not found in specimens examined immediately after quenching, but only after an ageing period. Such defects were not observed when the soaking at  $1200^\circ \text{C}$ . was carried out *in vacuo* or in nitrogen, followed by water-quenching. The conclusions are therefore drawn that the cracks cannot be due solely to the stresses resulting from the drastic heat treatment and that



hydrogen must be regarded as the major factor operative in hair-line crack formation.

Evidence was obtained that when cracks had been formed they contained hydrogen. Thus, as a result of rapid heating to 300° C., white ferrite veins surrounded the cracks, whilst after similar rapid heating to 650° C. globular carbides were observed instead. The suggestion is made that the white ferrite veins are due to decarburisation by the hydrogen contained in the cracks immediately after formation. Decarburisation results in the formation of methane, which is increasingly unstable above 600° C. in contact with steel. Accordingly, rapid heating to 650° C. results in the precipitation of carbide on the surfaces of the crack. It is therefore to be concluded that carbide segregation along the cracks is a result and not the cause of cracks.

In addition to the white veins of ferrite surrounding the cracks in tempered specimens, quite distinct white filaments of an austenitic character were observed in hydrogen-treated and quenched specimens. The gradual disappearance of these white filaments at room temperature is in keeping with the view that they consist of a hydrogen-rich constituent which owes its stability, at any rate in part, to its hydrogen content.

## FORGING, STAMPING AND DRAWING

(Continued from pp. 140 A-141 A)

**Making Tractor Forgings.** H. Chase. (Metals and Alloys, 1942, vol. 15, June, pp. 956-961). The author gives an illustrated description of the forging shop and sequence of processes at the tractor works of the International Harvester Co. in Chicago.

**Steels for Plastic Molding.** J. Delmonte and W. Renwick. (Iron Age, 1942, vol. 149, May 28, pp. 52-55). The authors discuss the design of multi-cavity moulds for the mass production of articles made of plastics and consider the properties of the steel from which they are made.

**Air Hardening Steels for Inert Drop Forging and Press Forging Dies.** H. E. Replogle. (Heat Treating and Forging, 1942, vol. 28, May, pp. 225-227, 234). The author describes the design, hardening treatment and tempering of inserts for drop-forging and press-forging dies of two 5%-chromium steels, one containing 0.35% of carbon and the other 0.95% of carbon.

**The Shape of the Walls of Forgings and Dies.** P. Patek. (Heat Treating and Forging, 1942, vol. 28, May, pp. 230, 240-241). The author discusses factors affecting the design of forging dies with special reference to the amount of taper on the sides of projections and recesses.

**The Upsetter.** A. F. Macconochie. (Steel, 1942, vol. 111, July 13, pp. 78-79, 105). The author briefly describes and illustrates the sequence of processes in the manufacture of ball-race rings, railway fittings and other small parts in upset forging machines.

**The Heating-Up of Wire and Die in Cold-Drawing.** A. Eichinger and W. Lueg. (Iron and Steel Institute, 1942, Translation Series, No. 99). An English translation is presented of the authors' paper describing their method of measuring the amount of energy converted into heat in the cold-drawing of wire. (*See* Journ. I and S. I., 1942, No. I., p. 183 A).

## HEAT TREATMENT

(Continued from pp. 143 A-144 A)

**Automatic Heat-Treating Furnaces Speed Production of Aircraft Parts.** (Industrial Heating, 1942, vol. 9, Mar., pp. 292-294). Some electric furnace installations for the heat treatment of aircraft parts in protective atmospheres are described and illustrated. Large parts are treated at the rate of 500 lb. per hr. in trays pushed through the furnace by a hydraulic ram. Smaller parts are hardened at the rate of 100-125 lb. per hr. by passing them through a two-zone furnace, 4ft. 6in. long, on a belt conveyer.

**"Tailor-Made" Gears Produced at New Sier-Bath Plant.** (Industrial Heating, 1942, vol. 9, Mar., pp. 316-320). A brief illustrated description is given of the heat-treatment plant of the Sier-Bath Gear Co., at North Bergen, New Jersey, with which gears are carburised in an atmosphere formed by cracking a suitable oil.

**Heat-Treating Jack Parts.** (Machinist, 1942, vol. 86, July 18, p. 296). An illustrated description is given of the heat-treating department of the American firm Templeton Kenly & Co., where parts for lifting jacks are hardened in salt-bath furnaces.

**Application of Controlled Atmospheres to Heat Treating.** C. E. Peck. (Metal Progress, 1942, vol. 41, June, pp. 814-818). The author describes equipment for the preparation of the following types of controlled atmosphere for heat treatment: (1) Completely burned fuel; (2) partially cracked fuel; (3) completely reacted fuel; (4) type (1) with the carbon dioxide and moisture removed by scrubbing; (5) type (2) with the carbon dioxide and moisture removed by scrubbing; (6) dissociated ammonia; (7) type (6) completely burned; and (8) type (6) partially burned. Data are also presented on the approximate cost, composition, dew point and suitable and unsuitable applications of these atmospheres.

**Nitrided Cast Iron as an Alloy Steel Substitute.** B. Thomas. (Metallurgia, 1942, vol. 26, July, pp. 87-88). The author describes some tests on the use of nitrided cast iron for clipping tools to remove

the flash from drop forgings. After rough-machining, the casting was first treated by heating slowly to  $900^{\circ}\text{C}$ . and cooling in a weak air-blast; finish-machining was then executed and a slight radius given to any sharp corners. Nitrogen hardening was carried out as for steel by heating for 90 hr. at  $500\text{--}510^{\circ}\text{C}$ . There was no distortion during production, and tools made in this manner have given extremely good service.

**Metallurgical Control of Induction Hardening.** F. F. Vaughn, V. R. Farlow and E. R. Meyer. (Transactions of the American Society for Metals, 1942, vol. 30, June, pp. 516–538). The authors report on an investigation of the effects of changes in the power input and duration of current flow on the hardness and microstructures of carbon steels heat-treated by the induction-hardening process using 3000-cycle H.F. current. The general conclusions reached were: (1) The maximum surface hardness attainable is a function of the carbon content, and, consistent with obtaining a proper metallographic structure, the maximum value increases from Rockwell C 61 for 0.35% carbon steel to Rockwell C 68 for 0.70% carbon steel; (2) the optimum depth of hardness, using 3000-cycle H.F. current, lies in the range 0.125–0.150 in., and this is governed by the metallographic limitations of (a) incomplete solution for shallow depths, and (b) grain growth and coarsening for greater depths; (3) the input of electrical energy is proportional to the volume of metal hardened, and this relationship can be expressed by the equation  $V = 0.0024P - 0.12$ , where  $V$  is the volume of metal hardened and  $P$  is the power input in kilowatt-seconds; this applies to a steel with a hardenability of 43.6 Rockwell inches; (4) to harden unit length of a round bar to a given depth, the power input required increases directly with the bar diameter; and (5) for a given diameter of bar and power input, a change of 1 Rockwell inch in the hardenability of the steel increases the depth of the hardened zone by approximately 0.0025 in. (Note: The Rockwell-inch unit of hardenability is the Rockwell hardness ( $C$  scale) on the surface of a 1-in.-dia. bar, 1 in. from the end, in the Jominy end-quench test.)

## WELDING AND CUTTING

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(Continued from pp. 144 A–146 A)

**The Economical Use of Arc-Welding Electrodes.** (Engineering, 1942, vol. 154, Aug. 14, pp. 126–127). Recommendations are made on the welding conditions which should be maintained to ensure good-quality arc-welds combined with the economical use of the electrodes. Illustrations and tables are presented which show the effects of low and high welding speeds and of low and high voltages and currents.

**Weld Hardening and Steel Composition.** A. Edson. (Metals and Alloys, 1942, vol. 15, June, pp. 966-971). The author has carried out hardness surveys across sections of  $\frac{1}{2}$ -in. steel plates on which a bead of weld metal was deposited under uniform welding conditions. Standard mild-steel coated electrodes were used for all the welding, but a variety of low-alloy steels were used as base-plates, the object being to relate the maximum hardness of the heat-affected zone to the composition of the plate. From the data obtained the author develops an equation which expresses the logarithm of the Vickers hardness number in terms of the contents of carbon, manganese, nickel, chromium, molybdenum, vanadium and copper in the base-plate. The equation is valid up to certain maximum contents of these elements for the welding conditions described.

**Spot Welding in Mild Steel.** (Engineer, 1942, vol. 174, Aug. 14, pp. 132-133). This article is an abridged version of Welding Memorandum No. 8 issued by the Department of the Controller-General of Research and Development, Ministry of Supply. It summarises the factors affecting the quality of spot-welds and suggests methods of controlling and inspecting the quality.

**Welding Stainless Pressure Vessels.** G. H. Sandberg. (Machinist, 1942, vol. 86, July 18, pp. 293-295). The author describes the welding of a stainless steel heat exchanger 54 in. in dia. and 22 ft. long with a shell-plate  $\frac{3}{4}$  in. thick and tube-plates 4 in. thick, with particular reference to preparation of the surfaces by machining and setting-up for welding.

**The Bronze-Welding of Cast Iron.** T. J. Palmer. (Machinery, 1942, vol. 61, July 23, pp. 100-103). The author describes the technique of preparing and bronze-welding fractured iron castings, stressing the importance of removing grease and oil which may have penetrated into the metal and of cutting a wide V to receive the bronze.

## CLEANING AND PICKLING OF METALS

(Continued from p. 112 A)

**Metal Cleaning.** R. W. Mitchell. (Iron Age, 1942, vol. 149, May 14, pp. 49-51). Owing to the shortage of chlorinated solvents for cleaning metals, substitutes are being used in the United States. In this paper the author discusses the properties of two proprietary concentrated emulsifiable solvent cleaners which are diluted with paraffin and can be used for loosening dirt and grease. The dirt is subsequently removed by jets of water under pressure. Simple equipment for cleaning small parts in trays and for shells is described and illustrated.

**Scarfig High Carbon and Alloy Steels.** G. D. Winlack. (Iron and Steel Engineer, 1942, vol. 19, Apr., pp. 26-33). The author



discusses the process and advantage of oxy-acetylene descaling or scarfing for removing surface defects from billets. He points out the necessity for preheating billets of high-carbon and alloy steels up to 400° F., allowing a minimum preheating time of 2 hr. for bars  $2 \times 2$  in. and 5 hr. for blooms  $10 \times 10$  in.

**The Cleaning and Degreasing of Metals before the Application of Organic and Inorganic Coatings.** H. Rogner. (*Korrosion und Metallschutz*, 1941, vol. 17, June, pp. 204–207). The author reviews the chemical and mechanical methods used in practice for cleaning and degreasing metal surfaces before coating. He points out that for technical and economic reasons, treatment with inorganic solutions is in most cases preferable to that with organic solutions, and he deals at some length with various techniques for applying the former.

**The Descaling of Steel by Pickling in Acids.** W. O. Kroenig and E. M. Saretzky. (*Korrosion und Metallschutz*, 1941, vol. 17, July, pp. 243–246). In order to prove that pickling is an electrochemical process, the author studied the behaviour of a steel/10%– $\text{H}_2\text{SO}_4$ /oxidised-steel electric cell. The investigation led to the following conclusions regarding the phenomena involved in the pickling process: (1) Pickling is based on an electrochemical dissolution of steel and a reduction of the higher oxides to ferrous oxide by the hydrogen liberated. Ferrous oxide is dissolved by the acid, and thus causes the scale to break off from its base. (2) It is mainly  $\text{Fe}_3\text{O}_4$  which is reduced, and which is effective as a depolariser. Practically no  $\text{Fe}_2\text{O}_3$  is reduced. (3) Unless there is some contact between the electrolyte and the metal surface covered by the scale, no hydrogen will be liberated at the cathode, no gaseous hydrogen being given off at the scale. (4) The liberation of hydrogen at the anode is due to local cells. (5) The rate of descaling is mainly controlled by the cathode potential. (6) After the reduction of  $\text{Fe}_3\text{O}_4$  the current intensity of the steel/acid/scale cell decreases considerably. (7) The following three-electrode cell is effective in the pickling process: Fe (cathodic areas)–Fe (anodic areas)–scale. (8) The loss in weight of the anode due to contact with a scale layer of the same area is less than 10% of the total quantity of dissolved anode metal.

## COATING OF METALS

(Continued from pp. 113 A–117 A)

**Determining Surface Area of Stampings.** N. Hall. (*Metal Finishing*, 1941, vol. 39, Dec., pp. 662–665). The author presents three charts for the rapid determination of the surface area of stampings, given the weight of a sample in ounces or grammes and the gauge of the material. The charts are for copper, brass and

steel respectively : they are simple to use, and assist in making cost calculations in the electroplating industry.

**The Application of Electrolytic Chromium for Corrosion Resistance.** K. Gebauer. (*Korrosion und Metallschutz*, 1940, vol. 16, Sept., pp. 297-299). The author discusses the appearance and properties of chromium coatings electrolytically deposited directly on to iron and steel. To produce a non-porous and crack-free chromium coating it is necessary for the base metal to be clean and as far as possible free from pores and slag inclusions. Experience has shown that to produce dense coatings the surface should be ground, polished and given an anodic etching. A network of very fine almost invisible cracks is found on all chromium coatings; their width is of the order of about  $10^{-5}$  mm. It is possible under certain conditions to produce crack-free coatings, but they are not very good as protection against corrosion because under heat stresses the stress distribution is uneven; when subjected to heat, cracks form which are some distance apart, are visible to the naked eye and extend right through the coating to the base metal.

**Temperature Control for Chromium Plating.** L. B. Lumpkin. (*Metal Finishing*, 1942, vol. 40, June, pp. 302-304). The author points out that accurate control of temperature in chromium-plating baths is essential if uniform deposition of the metal is to be obtained. He describes with drawings electrically operated and pneumatic control systems and discusses the advantages and disadvantages of each.

**Distribution of Nickel Electroplate over Irregular-Shaped Articles.** E. E. Halls. (*Metallurgia*, 1942, vol. 26, July, pp. 77-79). The author describes briefly the stripping method of determining the thickness of a nickel coating on steel, which yields an average thickness value for the part in question, and the British Non-Ferrous Metals Research Association jet test (known as the "B.N.F. jet test"). Some tests were made to reveal the changes in thickness at different positions on square panels, and it was found that : (1) In general, the thickness was least at the centre; (2) thicknesses of different order existed on opposite sides of the same panel; and (3) shielding effect, due to overlapping, was apparent. Some data are presented which illustrate the distribution of nickel plating on a length of channel section, on short round steel bars and on an L-shaped rectangular bar.

**Accelerated and Retarded Phosphatising Methods.** W. Machu. (*Korrosion und Metallschutz*, 1941, vol. 17, May, pp. 157-174). The author reports on a quantitative examination of all those phosphatising baths to which accelerators are added in order to shorten the phosphatising period. The investigation, which included the study of the porosity of the phosphate layer, of the variation of the potential during the treatment, of the pore resistance and of the thickness of the phosphate layer, led to the following conclusions : (1) The study of the effect of additions of nitrate, nitrite, bichromate,

bisulphite, copper salts, quinoline, and various inhibitors and accelerators on the free pore area and on the variation of the potential during phosphatising showed that the porosity of the phosphate layer is only very slightly increased by the presence of these accelerators. (2) The simplest means of establishing the end-point of phosphatising is the observation of the potential of the treated material, since the time-potential curve strictly obeys the Müller auto-passivation law. (3) Even in the presence of accelerators, the phosphatising time is more than doubled after pickling. (4) The thickness of the phosphate layer can be deduced from the current-time curve; for bonderised and Granodine layers  $2.2 \times 10^{-3}$  and  $1.3 \times 10^{-3}$  cm. respectively were found. (5) The protective value of the phosphate layer cannot be improved by continuing the phosphatising treatment after the free pore area and the potential have become constant. (6) The pore resistance of the phosphate layer is about 2000 ohms also in phosphatising baths containing accelerators. (7) The addition of oxidising agents in too high concentrations does not result in an acceleration of the phosphatising process, since, owing to passivation of the iron, no phosphate layer is formed at all. (8) The phosphatising process is accelerated not only by oxidising but also by reducing agents, such as sulphurous acid and salts of metals nobler than iron, *e.g.*, copper, lead, silver, mercury, and also by organic inhibitors, such as quinoline, dibenzyl sulphoxide and Rhodine. (9) That these chemically dissimilar substances are all effective as accelerators is due to the fact that phosphate is deposited at local cathodes only, dissolution of iron taking place at the local anodes. The phosphatising process must thus be considered as a combination of topochemical and electrochemical reactions. The accelerators enlarge the local cathode areas, and at the same time decrease the centres acting as anodes. All measures which increase the ratio of the cathodic to the anodic areas accelerate the phosphatising process. (10) Cathodic polarisation of the treated material accelerates and anodic polarisation delays the phosphatising process. Polarisation by alternating current has an accelerating effect, since the cathodic current impulse is more effective than the anodic one. (11) Anodic treatment in acid phosphatising baths does not result in the deposition of secondary zinc or manganese phosphates but in the formation of primary soluble iron phosphate, which lowers the protective value of the coating. (12) Assuming that insoluble zinc and manganese phosphates are deposited at the local cathodes only, the author's electrochemical theory of the effect of accelerators explains in a simple way the effect of oxidising and reducing agents as well as of metals nobler than iron, of organic inhibitors and of the application of electric current on the deposition of phosphate.

**Composition and Effect of Phosphatising Systems.** G. Roesner, L. Schuster and R. Krause. (*Korrosion und Metallschutz*, 1941, vol. 17. May, pp. 174-179). The authors discuss the equilibrium conditions prevailing in various phosphatising systems used in



practice, dealing separately with manganese phosphate baths, zinc phosphate baths and baths containing accelerators. In the last group particular consideration is given to baths with oxidising agents. The authors point out that phosphatising baths are effective only for a very limited period unless oxidising agents are added, and of these, nitrates and nitrites are most suitable since they do not give rise to any undesirable secondary reaction. The compositions and properties of some nitrate-containing phosphatising systems are dealt with at some length with especial consideration to the Bonderising process.

**The More Recent Phosphate Rust-Proofing Methods with Special Reference to the Patent Literature.** H. Högel. (Korrosion und Metallschutz, 1941, vol. 17, May, pp. 180-188). The author reviews the development of the phosphatising process since 1933, dealing in separate paragraphs with the following subjects: Cleaning and rust removal with phosphoric acid; treatment of the metal surface before phosphatising; composition and preparation of the phosphate baths; modifications of the phosphatising technique; regeneration of the phosphate baths; subsequent treatment; phosphate treatment of non-ferrous metals; special applications of phosphatising; and, paints containing phosphoric acid. In conclusion, a chronological list is given of 123 patents granted since 1933 in connection with the phosphatising process, German, U.S.A., Canadian, British, French, Indian, Austrian, Russian and Swiss patents being enumerated separately.

**A New, High Thermal-Conductivity, Protective Coating for Iron Condenser Tubes.** W. Wesley. (Korrosion und Metallschutz, 1941, vol. 17, May, pp. 188-190). The author reports on the formation of thin tightly-adhering coatings on iron tubes which, subsequent to phosphatising by the Atrament process, had been treated with water filtered through an aggregate called "Magno" (a mixture of calcium carbonate and magnesia). Coatings produced in this way are suitable for condenser tubes, since they are resistant to the attack of water containing calcium-carbonate and have a high thermal conductivity, *i.e.*, about 90% of that of iron.

**The Influence of the Post-Treatment of Phosphate Coatings on Their Protective Value.** W. Wiederholt, V. Duffek and J. Sonntag. (Korrosion und Metallschutz, 1941, vol. 17, June, pp. 193-203). The authors investigated the effect on the corrosion resistance of steel sheet of various treatments subsequent to phosphatising, *viz.*: (1) Rinsing with water and with dilute chromate solution; (2) treatment with various oils (the composition of which is not stated); (3) treatment with oils diluted with organic solvents; and (4) treatment with diluted oils containing some organic additions (paraffin wax, stearate and lanolin). The 55 × 110-mm. and 60 × 100-mm. sheet-metal specimens used for the investigation were phosphatised by an accelerated method and, after the post-treatment, were subjected to various corrosion tests, *viz.*, water- and salt-spray tests,



exposure in moist atmosphere, submersion in 1% potassium ferrocyanide solution and in 3% sodium-chloride solution. The two last tests served to reveal porosity. The results, *i.e.*, the period after which rusting started and the type of rust formation, are listed in six extensive tables. They lead to the following conclusions: (1) The protective value of the phosphate coating is improved by rinsing with water containing about 0.5 g. of sodium chromate per litre. (2) The corrosion resistance is further increased by subsequent treatment with oil, for which a dilution with organic solvents in the ratio 1:5 is recommended. (3) The effect of the oil treatment is improved by additions of paraffin wax, stearate or lanolin.

**The Phosphate Layer as a "Running-In Layer" for Piston Rings.** F. Bremer. (*Korrosion und Metallschutz*, 1941, vol. 17, June, pp. 208-209). The author briefly reports on the production of phosphate coatings on piston rings by a modified Atrament process, and on the advantages of such coatings during the running-in period, especially with the use of graphite as lubricant. The wear is stated to be considerably smaller than with non-phosphatised piston rings, and satisfactory sealing is attained after a short period.

**Phosphatising by Spraying as a Pretreatment to Lacquering.** W. Overath and L. Schuster. (*Korrosion und Metallschutz*, 1941, vol. 17, June, pp. 209-211). The authors emphasise the importance of suitable preliminary treatment of the steel surface before the application of lacquers, especially those with a synthetic-resin base. They point out that a phosphate layer between the steel surface and the lacquer film prevents rusting under the film and, in addition, its adherence and durability are increased. The phosphate layers should be as thin and fine-grained as possible, and to achieve this they recommend producing them by a modified Bonderising process, described in the paper, the characteristic of which is that the phosphate solution is sprayed on to the articles to be treated.

**Facilitating Cold-Working by Phosphatising.** H. Faber and H. Kopp. (*Korrosion und Metallschutz*, 1941, vol. 17, June, pp. 211-214). The author discusses the technique and the advantages of the Singer process, *i.e.*, a process, patented several years ago in Germany, Great Britain and other countries, in which a phosphate coating is applied to steel articles before they are cold-worked, especially before drawing. The main advantages claimed are that intermediate annealing can be dispensed with and that the tools and dies have a long life.

**A Survey of Galvanic Methods of Coating Stainless Steel.** H. Krause. (*Korrosion und Metallschutz*, 1940, vol. 16, Sept., pp. 304-308). For certain articles it is sometimes desirable to deposit a coating of another metal on stainless steel, as for instance copper on the bottom of stainless-steel cooking utensils. In this paper the author reviews old and recent electrolytic methods of depositing metallic coatings on stainless steel. It is no longer considered necessary to use concentrated acid baths for such coatings. A

larger addition of chlorides than that usually made to nickel baths (but not ammonium chloride) had a definite favourable effect on the plating process; organic acid additions are also beneficial. In cases where an intermediate nickel coating prior to a silver deposit is wanted, the nickel deposit must be very thin, even less than 0.001 mm.

**The Production of Coatings of Copper and Copper Alloys by Non-Galvanic Methods.** W. Machu. (Korrosion und Metallschutz, 1940, vol. 16, Sept., pp. 308-314). The author reviews the following methods of coating iron and steel with copper and copper alloys: (a) Dipping in molten copper in a closed vessel containing an inert atmosphere; (b) diffusion or cementation processes; (c) hot and cold rolling processes; (d) lining the mould walls with copper sheet and pouring the molten iron or steel into it; and (e) metal spraying.

**The Addition of Alloying Elements to Hot-Dip Galvanising Baths. Part I. Effect on the Structure.** H. Bablik. (Korrosion und Metallschutz, 1940, vol. 16, June, pp. 203-206). The author discusses the effects of the presence of small quantities (up to 1.5%) of lead, cadmium, iron, tin, aluminium and antimony in the molten zinc bath on the structure and appearance of galvanised coatings.

**The Addition of Alloying Elements to Hot-Dip Galvanising Baths. Part II. Effect of Iron Solubility.** H. Bablik and F. Götzl. (Korrosion und Metallschutz, 1941, vol. 17, Apr., pp. 128-130). The authors consider how the presence of alloying elements in a hot-dip galvanising bath affect the iron or steel to be galvanised and the material of which the kettle is made. They conclude that, with the exception of aluminium, the addition of other alloying elements has no effect on the solubility of the iron in the article being coated. As to the life of the kettle, small additions of copper have no effect; lead and tin additions are detrimental, and antimony and cadmium are exceedingly detrimental.

**Regalvanizing Welded Seams.** (Steel, 1942, vol. 110, June 29, pp. 64-66). When a galvanised steel structure is welded the zinc coating at and adjacent to the weld is destroyed. In this article brief particulars are given of a method of regalvanising these areas. While still hot from the welding the joint is cleaned with a wire brush and the surface is rubbed with a bar of a low-melting-point galvanising compound; the molten compound is then spread evenly over the hot surface with the same wire brush.

**The Behaviour of Malleable Iron in Contact with Molten Zinc.** F. Roll. (Korrosion und Metallschutz, 1940, vol. 16, June, pp. 206-207). It has been observed that cast iron high in silicon is strongly attacked by molten zinc and that it is therefore an unsuitable material for making cast galvanising baths. In this paper the author reports on tests to determine the behaviour of white-heart and black-heart malleable cast iron (silicon 0.45% and 0.98% respectively) in molten zinc. The results of loss-in-weight and tensile tests are given, and these demonstrate that black-heart malleable

cast iron has a heavy] corrosion loss, whilst white-heart iron is a suitable material for zinc baths at up to 470° C., provided that the carbon content is very low.

**Practical Problems in Electrotinning.** S. Baier. (Metal Industry, 1942, vol. 60, June 26, pp. 435-438; vol. 61, July 10, pp. 25-28). The author gives comprehensive descriptions of the process of electrotinning steel and other metals in alkaline stannate baths worked hot and in acid sulphate baths worked cold, and discusses the difficulties most frequently met with.

**The Effect of "Alumetised" Layers on the Scaling and Growth of Cast Iron.** F. Roll. (Korrosion und Metallschutz, 1941, vol. 17, July, pp. 247-249). The author studied the behaviour of six qualities of cast iron sprayed with aluminium by the Schoop method when heated at 850° C. in air, nitrogen, ammonia and carbon dioxide. He found that neither scaling nor growth was reduced by the coating.

**Colouring Armament Components.** (Machine Shop Magazine, 1942, vol. 3, June, pp. 40-41). Some particulars are given of a method of imparting a black finish to iron and steel such as is sometimes required for parts of weapons. The parts must first be degreased, and the colouring is done by immersing them in two baths prepared by dissolving proprietary powders in water; the time of immersion varies from 8 to 30 min. in each tank, according to the quality of finish required.

**Protective Coatings for Steel.** C. H. Ellaby. (Engineer, 1942, vol. 174, Aug. 7, p. 122). The author gives an account of his experiments with different combinations of paints which were made in order to select a suitable protective coating for the steel control gates on the dams and locks of the Upper Mississippi River. These gates were subject to alternate wetting and drying and to the abrasion of solids carried in the water. After seven years of extensive investigations the author concludes that an economical, durable and satisfactory protection for steel for the service in question can be achieved with materials now available. He recommends the following procedure: (1) Complete removal of all mill scale, either by acid-pickling or sand-blasting; (2) treating the newly cleaned surfaces with a phosphoric-acid/sodium-dichromate solution; and (3) applying at least three coats of a synthetic-phenol-resin/tung-oil-varnish vehicle paint pigmented to suit the particular conditions existing. The vehicle is all important, as was shown by the fact that, of numerous test panels, the two with the best corrosion resistance were both made with the same vehicle (phenol-formaldehyde resin varnish), and one contained the cheapest pigment (largely iron oxide) and the other the most expensive pigment (aluminium).

**Priming Paint (Lead Base) for the Protection of Steel Sheet.** (British Standards Institution, War Emergency Standard No. 1033-1942).

## PROPERTIES AND TESTS

(Continued from pp. 146 A-152 A)

**Properties of High-Purity Iron.** H. E. Cleaves and J. M. Hiegel. (Journal of Research of the National Bureau of Standards, 1942, vol. 28, May, pp. 643-667). The authors report the results of their determinations of the hot- and cold-working characteristics, microstructure, and density, and the thermal, electrical and magnetic properties of iron of high purity in which the maximum amount of any impurity was 0.004% and in which the total impurities did not exceed 0.01%.

**Mechanical Detection of Wheel-Seat Flaws in Railway Axles.** F. C. Johansen. (Engineering, 1942, vol. 154, Aug. 7, pp. 101-104). The author describes the testing equipment and procedure devised by the London Midland and Scottish Railway Co. for testing axle and wheel assemblies for fatigue cracks which sometimes develop close to the inner end of the press-fitted wheel-boss. A wholly mechanical arrangement was developed, depending on the principle that the deflection under load of a short length of the axle is greater if that length includes a flaw than if it is sound. The test is carried out without having to press the wheel off the axle. Under the normal loading system a downward force upon each journal is balanced by an equal upward reaction at each wheel, and the axle is bent upwards in the middle, suffering a continuous change of slope throughout its effective length. This change of slope near the inner end of the wheel-boss is measured by means of a dial-gauge mounted on a radial arm, so that the end of its plunger rests on the inner face of the tyre on the wheel. The apparatus in its final form has three radial arms, making two 60° angles, fixed to a split ring which is clamped round the axle. By observing the changes in the readings of the three dial-gauges with different positions of the axle relative to the load, the position of a flaw can be deduced.

**The Quenching of Steel after Tempering and the Impact Test.** L. E. Benson. (Engineering, 1942, vol. 154, Aug. 14, pp. 134-135). The author describes an investigation of the failure of gear-wheel teeth of nickel-chromium steel which had been quenched after tempering following hardening. The obvious fatigue character of the primary cracks suggested that failure occurred through repeated overloading in service, but other evidence came to light which was not in agreement with this theory. It was established that the quenching after tempering at 600° C. set up high internal stresses in the material which lowered its resistance to the external stresses applied in service. Apart from failure in service, the stresses set up by quenching after tempering are certainly responsible for great trouble in machining owing to the distortion which accompanies the redistribution of stress. The author deprecates the practice of



quenching after tempering in order to increase the impact value, for it is probably no exaggeration to say that a minimum Izod figure of 10 ft.lb would provide an adequate safeguard for general engineering purposes where an impact figure is required at all.

**Fatigue Strength of Crankshafts.** C. G. Williams and J. S. Brown. (Institution of Automobile Engineers : Engineering, 1942, vol. 154, July 17, pp. 58-59 ; July 24, pp. 78-80). In this report on the fatigue testing of full-size crankshafts for compression-ignition engines the authors first describe the testing machines used, which were of the constant-strain type, the object being to apply repeatedly a known bending movement to one crank-throw at a time and thereby to obtain as many fatigue tests as possible from one multi-throw shaft. Six designs of chromium-nickel steel crankshaft were tested ; in one case shafts of the same design in two steels of different tensile strengths were available. The results indicated that the decrease in fatigue strength, due to the use of a steel of lower tensile strength, was almost in proportion to the reduction in tensile strength. The effect of various methods of surface hardening on the fatigue strength was also examined. Chromium-plating was found to have a marked detrimental effect in reducing the fatigue strength. Induction hardening treatment caused, in general, a loss of fatigue strength, the results being erratic ; this reduction in fatigue strength was attributed to the residual stresses induced adjacent to the hardened zone, but it is possible that induction hardening may be detrimental if the maximum applied stress is just outside the hardened zone, but may be beneficial if the point of maximum stress is within the hardened zone. Tests with nitrided shafts revealed that these had an appreciably greater fatigue strength, the increase being of the order of 25-60%. This is probably largely attributable to the compressive stresses induced by nitriding.

**The Influence of the Combination of Principal Stresses in Fatigue of Metals.** D. J. McAdam, jun. (American Society for Testing Materials, June, 1942, Preprint No. 32). The author surveys his recently published views on the influence of the combination of principal stresses on the technical cohesive strength and yield strength of metals. He then compares the diagrams representing these relationships with data published by various investigators on the influence of the combination of principal stresses on the fatigue limit. "Chafing fatigue" is considered to be a manifestation of the influence of combined radial compression and cyclic flexure. The author interprets the damaging effects of radial compression by reference to diagrams representing the influence of the combination of principal stresses on the technical cohesion limit.

**The Determination of the Solubility of Hydrogen in Iron and Iron Alloys.** J. H. Andrew, H. Lee and A. G. Quarrell. (Iron and Steel Institute, 1942, this Journal, Section I.). The solubility of hydrogen in (i) iron, (ii) a low-nickel iron alloy and (iii) a nickel steel, at various temperatures has been determined by a method which is

described. It is shown that hydrogen has no effect on the critical change of iron, but in the case of the nickel-iron a sudden drop in solubility begins at a point corresponding to the peak on the thermal cooling curve and continues to a temperature of 475° C., which is 75° C. below the completion of the change. This phenomenon was much more marked with the nickel steel, a fact which supports the view that carbon plays an important part in the retention of hydrogen in steel.

**Uses and Possible Substitutes for Cobalt.** J. Koster and H. W. Davis. (Steel, 1942, vol. 111, July 6, pp. 80-81, 119-121). This paper constitutes a report prepared at the request of the War Production Board (U.S.A.). In it the present application of cobalt in steels and suggestions for possible substitutes are made. Tantalum, uranium and boron steels are not considered to be satisfactory substitutes for cobalt high-speed steels. It is almost impossible to find a substitute for cobalt in permanent magnet steels, but some saving in cobalt can be effected by using complex steels containing less cobalt, *e.g.*, one containing cobalt 15%, chromium 10% and carbon 0.9%. When it is possible to cast the magnet in the desired finished shape, nickel-aluminium alloys with no cobalt may be used to replace some of the low-cobalt steels now used.

**British Standard Specification for Manganese Steel Gas Cylinders for Atmospheric Gases.** (British Standard Institution, No. 1045—1942). This Specification forms one of a series of British Standards for gas cylinders based upon the recommendations of the Gas Cylinders Research Committee of the Department of Scientific and Industrial Research.

**British Standard Specification for Structural Steel for Ship-building.** (British Standard Institution, No. 13—1942). This Specification constitutes a revision of British Standard No. 13 originally issued in 1901 and last revised in 1910.

**War Emergency British Standard Specification for Mild Steel Wire for General Engineering Purposes.** (British Standard Institution, No. 1052—1942). This standard has been prepared to co-ordinate the requirements for wire for general engineering purposes and to provide a Standard which can be used by Government Departments. It covers wire in six different finishes and in sizes from 40 S.W.G. to  $\frac{9}{16}$  in. in dia. or equivalent cross-section.

**Services' Schedule of Carbon and Alloy Steels for Armaments and Vehicles (Excluding Major Gun Forgings, Armour and Shells).** (British Standards Institution, May, 1942, B.S./S.T.A.5). This Schedule is based on British Standard No. 970. It has been prepared as a statement of the general Service requirements for engineering steels to co-ordinate and simplify the materials aspect of current war-time manufacture.

## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 152 A-154 A)

**Storage of Metallographic Specimens.** (Metal Progress, 1942, vol. 41, May, pp. 651-654). Correspondence is published in which a number of American metallurgists describe the cabinets and desiccating agents they use for storing metallographic specimens.

**The Polishing of Steel by Electrolytic Methods.** C. B. F. Young and W. L. Bryteczuk. (Metal Finishing, 1942, vol. 40, May, pp. 237-241; June, pp. 306-308, 317). The authors describe a series of electrolytic polishing tests, using a photo-electric reflectometer, the object of which was to determine the optimum polishing conditions and to compare bath solutions. It was found that for preparing specimens for metallographic examination, a solution containing 76.5% of acetic anhydride and 18.5% of perchloric acid by volume gave a very high polish, but for commercial work as a preliminary to plating, a solution consisting of phosphoric acid 60%, sulphuric acid 20% and water 20% was most suitable. The apparatus used for the tests is described and suggestions for further experimental work are made.

**The Solubility of Carbon as Graphite in Gamma Iron.** R. W. Gurry. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1440: Metals Technology, 1942, vol. 9, Apr.). The author describes experiments undertaken to determine the solubility of graphite in austenite by carburising samples of carbonyl iron at 957° and 1110° C. The saturation points at these temperatures were 1.39% and 1.89% of carbon respectively. The maximum solubility of graphite in austenite, determined by a short linear extrapolation to 1135° C., the temperature of the iron-graphite eutectic, was 1.98%. The author also constructed a cementite-solubility curve, based on data from the literature, and consistent with the measured graphite solubility. The intersection of this curve with that for the solubility of graphite indicates that cementite is unstable below about 1280° C. relative to graphite and to austenite saturated with graphite.

**The Effect of Normal Elements and Alloy Elements on the Rate of Austenite Transformation in Cast Iron at Constant Temperature.** C. Nagler and W. P. Wood. (Transactions of the American Society for Metals, 1942, vol. 30, June, pp. 491-512). The authors describe an apparatus which they developed for measuring the rate of transformation of austenite in cast iron at high temperatures, and discuss the results obtained in tests in which the effect of various elements in the iron on the transformation rate was studied. The procedure was to heat a sample above the critical range for 1 hr., quench rapidly in a lead bath maintained at the desired sub-critical temperature, and finally quench in water; this was repeated with

fresh samples from the same source, the time in the lead bath being increased by a short interval each time. The lead was kept at the desired temperature in a resistance furnace, and the sample ( $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$  in.) was held between the horizontal poles of a transformer with primary and secondary coils outside the furnace. As the transformation took place, the magnetic permeability of the sample increased, thus causing an increase in the e.m.f. generated in the secondary coil; this increase in current was measured by taking ammeter readings every 2.5 sec. Transformation curves were drawn by plotting the current against time. The transformations studied were all at 1200° F. The authors' conclusions were: (1) The magnetic method is more rapid and more accurate than the metallographic method developed by Davenport and Bain; (2) decarburisation, the temperature at which the carbides dissolve and the holding time at that temperature all influence the rate of austenite transformation; (3) manganese, sulphur, molybdenum and nickel all retard the transformation of the austenite, molybdenum having a greater retarding effect than any other known element; (4) carbon and chromium carbide accelerate the austenite transformation; (5) phosphorus and silicon tend to retard the transformation rate; (6) the influence of the alloying elements on the rate of austenite transformation in cast iron is similar to that in the case of steel as determined by Davenport (*see* Journ. I. and S.I., 1940, No. I., p. 211 A), the difference being one of degree only; (7) elements promoting carbide formation tend to accelerate the transformation and graphitisers tend to delay it.

## CORROSION OF IRON AND STEEL

(Continued from pp. 154 A-157 A)

**The Atmospheric Rusting of Iron.** G. Schikorr. (*Korrosion und Metallschutz*, 1941, vol. 17, Sept., pp. 305-313). The author reports on an investigation of the atmospheric corrosion of iron sponsored by the Staatliche Materialprüfungsamt Berlin-Dahlem. Special consideration was given to the effect of the time of the year and the locality on the corrosion. Further, the influence of the rust coating on the further progress of the corrosion was studied. This was done by comparison of the quantity of rust on a specimen exposed without interruption for a year with the total rust on twelve specimens each of which was exposed for one month only. All tests were carried out with vertically-hanging small plates (45 × 30 mm. and 2-4 mm. thick) of several qualities of iron and steel which were ground with emery before exposure. The investigation led to the following conclusions: (1) The roughness of the specimen surface and the direction of the wind have hardly any effect on the corrosion. (2) There is a definite, though small, effect of the height above the



ground at which the specimens are exposed: Those exposed on towers and roofs show more rust than those near the ground, which is probably due to the fact that the wind brings less sulphur compounds to the latter. (3) The rate of rusting, as measured in Berlin, is five times greater in winter than in summer, since the atmosphere contains more waste fuel gases in winter and its relative moisture content is higher. (4) There is a close connection between the rate of rusting and the quantity of sulphur compounds in the air. (5) In tests extending over less than a month acceleration of rusting due to rust already formed was observed. After longer periods, however, often a distinct protective effect of the rust was observed, so that the rate of rusting may be halved. (6) The rusting per month of iron that is exposed to the atmosphere, but protected from rain, is about half that of iron exposed to rain. The protective value of this rust is so small, however, that the total annual formation of rust on iron protected from rain is almost as great as that on iron freely exposed to rain. This is thought to be due to the fact that the sulphur compounds absorbed by the rust of the non-protected specimens cannot be washed off by the rain, and thus accumulate. (7) In a study of the effect of local (non-climatical) conditions on the corrosion the purity of the air was found to be of great importance. Also in the study of the effect of the climate of various parts of Germany it was found that the main factor is the degree of purity of the air. The following average rates of rusting (in mm. per year) are quoted for North-West and Central Europe: (a) In very remote districts, 0.01; (b) in moderately populated districts, 0.01-0.05; (c) in residential districts of large towns and in medium-size industrial towns, 0.05-0.1; (d) in large industrial towns, 0.08-0.15; (e) near the coast, 0.06-0.17. (8) Phosphorus and copper contained in iron have usually a distinctly inhibitive effect on rusting, which is obvious even after only a month's exposure. (9) The resistance to rusting of cast iron during a monthly period is, if anything, greater than that of mild steel. The rust formed has little protective value, however, so that in tests extending over a year cast iron is corroded a little more than mild steel.

**Prevention of Rust on Steel in Storage.** E. Armstrong. (Metal Treatment, 1942, vol. 9, Summer Issue, pp. 3-10, 24). The author directs attention to the savings effected by preventing rust from forming on steel, particularly sheet and strip for mass producing small components by blanking, forming, pressing and welding. He then discusses the rust-prevention properties of greases, oils and mineral jellies, dealing specially with lanolin-base greases of different degrees of purity which have the best protective properties judged by the results of hot and cold humidity tests.

**The Effect of Biological Processes on the Destruction of Materials.** L. W. Haase. (Korrosion und Metallschutz, 1940, vol. 16, May, pp. 155-160). The author cites examples of the corrosion of metals

aggravated by biological phenomena in boiler water and cooling water, and describes the steps taken to deal with this form of corrosion.

**Characteristics of Microbiological Deposits in Water Circuits.** W. J. O'Connell, jun. (American Petroleum Institute, Proceedings of Eleventh Mid-Year Meeting, May, 1941, pp. 66-82). The author presents an outline of some theories offering possible explanations of some types of corrosion in water-circulating systems, describes the processes involved in the formation of microbiological deposits and gives the analyses of some characteristic deposits of this nature. He stresses the importance of having clean surfaces as the initial step to the successful application of corrosion-prevention and control methods. Consideration is given to some of the more important contributions to the knowledge of the ecology, morphology and physiology of specific organisms and groups of organisms. A classified bibliography with 132 references is appended.

**Corrosion Prevention on the Water Side of Refinery Equipment.**  
**A—Chemical Treatment of the Water. B—Use of Deaerator.** W. H. Attwill. (American Petroleum Institute, Proceedings of Eleventh Mid-Year Meeting, May, 1941, pp. 90-95). In the first part of the paper the author describes the results obtained at a Texas refinery from four methods of treating water to prevent the corrosion of condenser equipment. Sodium-hydroxide and sodium-silicate treatments resulted in little, if any, reduction in the rate of corrosion; chromate treatment, after 2½ years' use, has proved very effective; sodium hexametaphosphate as an inhibitor is now being tried, for it is less expensive than the chromate treatment.

In the second part a description is given of a mechanical de-aerator installed at a Texas refinery which removes 98% of the dissolved oxygen from the water passing through it. The de-aerator consists of a tower 6 ft. in dia. and 20 ft. high in which a high vacuum is maintained by a two-stage vacuum jet. The water passes down over a large number of trays of cypress wood. The installation of this equipment reduced considerably the corrosion in the entire water system. The capital cost was high, but the operating costs are relatively low, and after two years' operation, both initial and operating costs have been recovered by the saving in condenser-tube corrosion alone.

**Water-Side Corrosion of Refinery Condensing Equipment.** B. B. Morton. (American Petroleum Institute, Proceeding of Eleventh Mid-Year Meeting, May, 1941, pp. 48-55). The author discusses in general terms how the corrosion of metals in refinery condensing plant is influenced by the three important variables aeration, temperature and rate of flow of the cooling water, and cites some examples of the corrosion of cast iron and copper-nickel alloys in water on the coast of the Gulf of Mexico.

**Corrosion Due to Sulphite-Bearing Feed Water.** W. Wesly. (Korrosion und Metallschutz, 1940, vol. 16, May, pp. 145-150). The author reports on an investigation of the causes of corrosion of

parts of the high-pressure boiler-feed system at the Oppau works of the I.G. Farbenindustrie. This was found to have occurred after the sulphur-dioxide content had been raised from 5-10 to 20-30 mg. per litre. The trouble was overcome by replacing some of the parts liable to attack with material of greater corrosion resistance and by reducing the sulphur dioxide content. The corrosion caused by carbon dioxide in the condensate was countered by the addition of ammonia to the steam condensate system.

**The Activation of Passive Iron in Nitric Acid.—I.** K. F. Bonhoeffer. (*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1941, vol. 47, Feb., pp. 147-150). This is a preliminary report on an investigation described in more detail in two later publications. (See the two following abstracts).

**The Passivity of Iron and the Ostwald-Lillie Model of Nerve Conduction.—II. The Threshold Value of the Cathodic Activation.** H. Beinert and K. F. Bonhoeffer. (*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1941, vol. 47, June, pp. 441-450). The authors report on a study of the activation of passive iron in nitric acid by cathodic polarisation. They found that, provided that the current impulses are sufficiently short, the quantity of electricity required for activation is practically independent of the time of flow current. This quantity is of the order of magnitude of  $10^{-4}$  coulomb per sq. cm., i.e., the same order of magnitude as that required for the reduction of a monomolecular oxide layer. The quantity of electricity required is considerably increased by the presence of nitrous acid. Current densities below a certain limit do not cause activation, however long they may be applied. The minimum quantities of electricity (threshold values) required under various experimental conditions for the activation of low-carbon iron wires are presented in several tables and diagrams. The authors point out that the phenomena observed are of especial interest in connection with the study of nerve conduction with the aid of the Ostwald-Lillie model.

**The Passivity of Iron and the Ostwald-Lillie Model of Nerve Conduction.—III. Oscillographic Study of the Cathodic Behaviour of Passive Iron and Platinum in Nitric Acid.** H. Beinert and K. F. Bonhoeffer. (*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1941, vol. 47, July, pp. 536-545). The authors report on an oscillographic study of the effect of cathodic polarisation on the potential of passivated iron and—for comparative purposes—of platinum in nitric acid. The oscillograms obtained with several qualities of iron, and for various temperatures and acid concentrations, indicated that there is an intermediate potential between the passive and active state. The authors suggest that the intermediate potential is due to the reduction of a mono-molecular oxide layer on the surface of the iron.

**Electro-Galvanising in Acid and Alkali, Mat and Bright Plating Baths.** M. Schlötter and H. Schmellenmeier. (*Korrosion und*



Metallschutz, 1941, vol. 17, Apr., pp. 117-123). The authors describe an investigation of the causes of the different corrosion resistance of electrolytic zinc coatings. The behaviour of zinc coatings in 1*N* sulphuric acid was first determined by measuring the volume of hydrogen evolved over given periods of time and calculating the amount of zinc dissolved; from the data loss-in-weight/time curves were constructed. These indicated three phases of attack: (a) The induction period; (b) the period of chemical solution of the zinc; and (c) the electrochemical solution phase which begins when the acid has penetrated to the iron-zinc boundary layer. The present investigation deals with factors affecting the rate of solution in the second phase or "straight-line" period. Zinc coatings deposited in an alkali bath were more easily dissolved by acid than were those produced in an acid bath, and the converse applied when the specimens were subjected to alkali attack. As the types of zinc coatings produced in different types of bath have different potentials, a zinc which is difficult to dissolve chemically, *i.e.*, which has a low potential against iron, will also be difficult to dissolve electrochemically. Hydrogen evolution tests on a hammered, and on an unworked but otherwise identical zinc coating showed that the rate of attack was much greater in the former case, so that mechanical stresses on the zinc can have a marked effect on its corrosion resistance. The authors also examined the effect of the amount of zinc oxide in different zinc coatings on their solubility, and established that the solubility in acid decreased with increasing zinc oxide content. This is not due to its chemical properties, for ZnO is itself easily soluble, but it is due to a change in the crystal structure of the coating. From the results obtained the authors conclude that the atomic structure of electrolytic zinc is changed by the taking up of surplus anions from the bath and that these changes affect its resistance to corrosion.

**A Note on the Corrosion of Steels by Weathering and by Dilute Acids, with a Consideration of the Effect of Heat Treatment and Cold-Work.** W. Eilender, W. Geller and W. Ausel. (Korrosion und Metallschutz, 1941, vol. 17, Sept., pp. 314-319). The authors studied the corrosion of (a) steels of various compositions, and (b) steels of similar compositions but derived from different melts, when exposed to the atmosphere, to sea-water (intermittent immersion) and to the attack by 0.45*N* and 0.045*N* sulphuric acid, 0.61*N* hydrochloric acid, 0.87*N* acetic acid and 0.75*N* nitric acid. The behaviour of all steels was more or less the same in the atmosphere and sea-water, but considerable differences were observed on exposure to acids, the greatest being with 0.45*N* sulphuric acid. This acid was used for some additional tests, in which the effect of various heat treatments and of cold-rolling on the liability to corrosion was studied. The results showed that the inherent properties of the steels even after heat treatment greatly affect the corrosion resistance. Cold-rolling increased the liability to attack by sulphuric acid.



**Comparison of the Protective Value of Phosphate and Oxide Coatings.** V. P. Sacchi. (Korrosion und Metallschutz, 1941, vol. 17, July, pp. 236-241). The author subjected specimens with oxide and phosphate coatings to the Preece copper-sulphate test directly after coating and after exposure to the atmosphere. The specimens were subjected to various treatments, such as degreasing, sand-blasting, polishing, &c., but no details are given regarding the production of the coatings. In all cases better results were obtained with the phosphatised than with the oxidised specimens. The author expresses the opinion, however, that the behaviour in the copper sulphate test cannot be considered a criterion of the protective value of a coating.

**A Note on the Resistance of Austenitic Chromium-Nickel Steels to Nitric Acid.** A. Gotta. (Korrosion und Metallschutz, 1941, vol. 17, July, pp. 241-243). The author studied the resistance of several 18/8 chromium-nickel steels with silicon contents of about 0.1% and 0.5% to the attack by boiling concentrated nitric acid. The steels with 0.1% of silicon proved to be considerably more resistant than those with 0.5%, which leads to the conclusion that very low-silicon or, better, silicon-free steels would form a particularly suitable material for plant subjected to the attack of nitric acid.

**The Suitability of Electro-Galvanised Coatings for Protecting Iron Against Corrosion.** J. Korpium. (Korrosion und Metallschutz, 1941, vol. 17, Apr., pp. 123-127). The author discusses recent improvements in electro-galvanising and the improvements in the properties of the coatings obtained. In general, electrolytic zinc coatings offer a better resistance than cadmium to industrial and rural atmospheres, whilst there is little to choose between them as regards protection against sea-water. Distilled water attacks zinc coatings, but not cadmium. A zinc coating alone offers better resistance to atmospheric corrosion than zinc with a chromium plating on top.

**The Corrosion of Galvanised Vessels by Pig Food.** H. Bablik and R. Garzuly-Janke. (Korrosion und Metallschutz, 1941, vol. 17, Apr., pp. 131-133). Cases of pig-poisoning have been reported, the cause of which was said to be the food which had been prepared in galvanised boilers. In this paper the authors describe an investigation of this question. Their conclusion was that the steaming of swill of normal composition in galvanised boilers does not affect the health of pigs. But if decomposed vegetable matter is allowed to lie for any length of time in galvanised vessels, the acid attacks the zinc, and the zinc content of the prepared pig food can thus become dangerously high.

## BOOK NOTICE

(Continued from pp. 128 A-130 A)

MANLEY, R. G. "*Fundamentals of Vibration Study.*" With a Foreword by W. Ker Wilson. 8vo. Pp. xii + 128. Illustrated. London, 1942: Chapman and Hall, Ltd. (Price 13s. 6d.)

This attractive little volume deserves a warm welcome from the steadily increasing army of engineers and others whose work necessitates a thorough grasp of the basic principles underlying the theory of mechanical vibrations, but who are unable to devote sufficient time to master the subject by a detailed study of the more lengthy standard texts.

The author is to be congratulated on having eliminated all redundant material and condensed the essentials into a concise and readily assimilated form. His treatment of the subject, whilst essentially mathematical, is well tempered with physical interpretations of the results obtained, and great pains have been taken to ensure that, so far as possible, no statement is made without accompanying proof. A knowledge of differential equations is not presupposed, and the direct and concise method of operators is ably demonstrated, together with that of complex numbers. Even those whose mathematics have been allowed to "rust" will find little difficulty in following the theory, especially if reference is made to the three excellent little appendices. Of these, Appendix III., dealing with determinants and frequency equations, should prove particularly valuable, as it is remarkable how few engineers appear to appreciate to the full the labour-saving uses of the determinant in numerical computation. A pleasing feature is the use of a key list of symbols at the beginning of the book, but the reader is not expected to rely on this alone, since all symbols are introduced in the text. The diagrams and figures are unusually clear, and are well placed in relation to the subject-matter they are intended to illustrate.

The scope of the work, whilst necessarily limited, gives a thoroughly adequate introduction to the fuller texts. It embraces damped and undamped systems having a single degree of freedom, undamped systems with two and many degrees of freedom, also continuous systems with distributed inertia and elasticity, whilst the final chapter deals with complex vibrations and harmonic analysis. Particular emphasis is rightly laid on the question of resonance in relation to damping and type of excitation, whilst the author's approach to the modern conceptions of effective inertia and dynamic stiffness, especially as regards coupled systems, is original and easily understood.

The book can be confidently recommended to engineers who desire to make a true study of vibration and thus obtain a clear understanding of the causes of fatigue failure occurring in practice. This is surely preferable to a mere proficiency in the application of formulæ the physical meaning of which is not completely understood.

S. F. DOREY.

## ORES—MINING AND TREATMENT

(Continued from p. 131 A)

**Excavating Machinery in the Ironstone Fields.** W. Barnes. (Engineer, 1942, vol. 174, Aug. 7, pp. 108-111; Aug. 14, pp. 128-129; Aug. 21, pp. 144-146; Aug. 28, pp. 164-166). After a brief description of the geology and economic aspects of the open-cast ironstone workings of Lincolnshire and the Midland counties, the author gives more detailed descriptions of the steam navvies, the 2-, 3- and 4-belt conveyors, skip transporters and other plant used to remove the cover or overburden.

**Mining and Transportation Practice in Minnesota Iron Mines.** G. J. Holt. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1427: Metals Technology, 1942, vol. 6, Mar.). The author gives an account of the equipment and methods employed at the Minnesota iron-ore mines for the open-face mining of the ore. Data are presented on the number of steam locomotives, Diesel- and petrol-engine lorries used and on the thickness of overburden and distances hauled. Underground mining has been on the decline for several years, and even in the present war emergency no new underground mines have been opened.

**Dry Differential Grinding Tests of Carnotite Ores.** S. M. Shelton and A. L. Engel. (United States Bureau of Mines, 1942, May, Report of Investigations No. 3636). The authors present a report on dry-grinding methods of beneficiating carnotite ores. This ore is a canary-yellow crystalline mineral occurring in the Colorado-Utah district; it contains vanadium pentoxide, and the present investigation was undertaken to ascertain what degree of concentration could be obtained and whether the vanadium recovered would justify the cost.

**Concentration of Manganese-Bearing Ore from the Bynum Property, Walnut Grove, Ala.** T. L. Johnston, M. M. Fine and S. M. Shelton. (United States Bureau of Mines, Manganese Investigations No. 11, 1942, May, Report of Investigations No. 3637).

**Laboratory Experiments on Sulfur Dioxide-Sulphuric Acid Leaching of Black and Brown Manganiferous Iron Ores of the Cuyuna Range of Minnesota.** C. T. Anderson. (United States Bureau of Mines, Manganese Investigations No. 14, July, 1942, Report of Investigations No. 3649).

**Hydrometallurgical Studies of Manganese Ores—Electrodeposition of Manganese.** D. Schlain. (United States Bureau of Mines, Manganese Investigations No. 15, July, 1942, Report of Investigations No. 3651).

**Beneficiation of Oxide Manganese Ores from Las Vegas Wash, Nev.** S. R. Zimmerley, C. H. Schack and F. E. Thackwell. (United

States Bureau of Mines, Manganese Investigations No. 16, 1942, May, Report of Investigations No. 3647).

**Concentration of Wad Ore from the Ayedalotte Property, Batesville, Ark.** S. M. Shelton, M. M. Fine and R. B. Fisher. (United States Bureau of Mines, Manganese Investigations No. 17, July, 1942, Report of Investigations No. 3652).

**The Sintering Plant at Great Lakes Steel Corporation.** E. Fuller. (Iron and Steel Engineer, 1942, vol. 19, May, pp. 27-30). The author gives an illustrated description of the sintering plant at the Ecorse Works of the Great Lakes Steel Corporation; drawings of the plant layout are also presented. The sintering machine is of the continuous type, and is 51 ft. long  $\times$  6 ft. wide. There are six wind-boxes and 61 sintering bogies, each with a frame 6 ft.  $\times$  2 ft.; these bogies pass through the sintering tunnel at from 2.13 to 4.26 ft. per min. The plant was originally designed to produce 340 tons in 24 hr., but some alterations in design were made as a result of which the production has been stepped up to 900 tons in 24 hr.

**The Preparation and Smelting of Minette Ore and Blast-Furnace Flue Dust.** J. Paquet and M. Steffes. (Stahl und Eisen, 1942, vol. 62, July 23, pp. 621-631). The authors give an account of trials carried out at the works of the Aciéries Réunies de Burbach-Eich-Dudelange, Luxemburg, with different methods of crushing and sintering Minette ores and blast-furnace flue dust. Details are also given of the effects on blast-furnace production and fuel consumption of using the following ore charges: (1) Ore as delivered from the mines; (2) crushed ore with the addition of unsintered fines; (3) crushed ore by itself; and (4) crushed ore with the addition of different proportions of sintered fines and sintered flue dust. The operation and results achieved with a rotary-furnace sintering plant are presented and discussed from both the technical and economic points of view.

## REFRACTORY MATERIALS

(Continued from pp. 162 A-163 A)

**Silicon-Carbide Bricks in Melting Practice.** C. Bruchhausen. (Giesserei, 1942, vol. 29, June 12, pp. 208-211). The author reviews the properties of silicon-carbide refractory bricks which are being used as a substitute for sillimanite bricks. Bricks with medium silicon-carbide contents have properties equivalent to those of special high-alumina bricks, whilst those containing about 85% of silicon carbide have a refractoriness of Seger cone 40. Their cold-compression strength is about 1000 kg. per sq. cm.; the coefficient of expansion is very low and the thermal conductivity is comparatively high. The bricks should not be exposed to strongly oxidising gases.



Silicon-carbide bricks are advocated for lining crucible furnaces in which tool steel is made.

**A Note on a Quantitative Corrosion Test for Refractories.** J. F. Hyslop. (Transactions of the British Ceramic Society, 1942, vol. 41, June, p. 165). The author describes a method of testing the resistance of refractory bricks to corrosion by slags. The procedure is as follows: (1) Drill a hole  $\frac{1}{4}$  in. in dia. and  $\frac{1}{2}$  in. deep in the brick; (2) fill with a definite weight of slag; (3) heat for a given time at a specified temperature; (4) cool, refill with slag and reheat; (5) repeat this treatment a definite number of times; (6) invert the test-piece, set it over a crucible, raise it to the chosen slagging temperature and hold for a sufficient length of time for the slag to drain into the crucible; and (7) measure the volume of the corroded cavity by filling up with a liquid. Some of the results obtained on different kinds of brick using 1 g. of basic open-hearth slag are reported.

**Electric Furnace Study of the MgO-SiO<sub>2</sub> System.** R. R. Ralston and G. T. Faust. (Journal of the American Ceramic Society, 1942, vol. 25, July, pp. 294-310). The authors report on an investigation of the magnesia-silica system. Melts covering the entire range of compositions were prepared in a crucible having one graphite electrode projecting upward through the bottom and a second one which could be lowered into the crucible. Potter's flint (pulverised primary quartz) and magnesia were used as starting materials for one series of samples, and olivine, quartz sand and magnesite were used as materials of less purity to simulate commercial conditions. Chemical, spectrographic, petrographic, density and Seger-cone determinations were made on typical specimens selected from each melt. Periclase, forsterite and clinoenstatite crystallised in strict agreement with the phase diagram, and the phenomenon of immiscible silicate phases was observed in high silica compositions. No new compounds were seen. Numerous fusions of natural olivine were made to determine the character of the product that could be produced by an electric furnace. The iron content was reduced to a very small quantity, ranging from 0.11% to 0.68% of FeO, some of which was contributed by ferrosilicon; this was a decided improvement over natural olivine, which contains 8.0% of iron oxide (calculated as Fe<sub>2</sub>O<sub>3</sub>).

## FUEL

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(Continued from pp. 163 A-166 A)

**The Gasification of Solid Fuels in Small Producers. Part I.—Gasification of Low-Temperature Coke in an Up-Draught Gas Producer.** E. Rammler, K. Breitling and J. Gall. (Iron and Steel Institute, 1942, Translation Series, No. 106). An English transla-

tion is presented of Report No. D83 of the Reichskohlenrat in Berlin, which was issued in December, 1938.

**Dust Problems in Burning Blast-Furnace Gas under Steam Boilers.**

A. R. Mumford. (Combustion, 1942, vol. 13, May, pp. 35-37). The author discusses data obtained in the course of a survey of steam boiler installations where blast-furnace gas is the fuel. Dirty blast-furnace gas when used alone is satisfactory for burning under boilers, even if these have refractory settings. When a supplementary fuel, such as oil or pulverised coal, is employed, the higher gas temperature may cause the dust to fuse and cause slagging on the heating surfaces; in such cases a separate combustion zone is desirable. Very often the cost of boiler cleaning is so low that it is more economical to burn dirty gas and clean the boilers than to erect and maintain a primary gas-washer.

**Technical and Economic Study of Drying Lignite and Sub-bituminous Coal by the Fleissner Process.** L. C. Harrington, V. F. Parry and A. Koth. (United States Bureau of Mines, 1942, Technical Paper No. 633). The authors report the results of trials of the Fleissner process of drying sub-bituminous coals and lignite with high-pressure saturated steam using a pilot plant capable of drying 1 ton of coal in two 8-hr. shifts. These trials showed that American coals high in moisture can be successfully dried by this process, which increases their gross heating value by 30-50%.

**Effect of Rate of Operation in the Coke Plant.** B. J. C. van der Hoeven. (Iron and Steel Engineer, 1942, vol. 19, June, pp. 68-74). The author discusses how changes in the coking rate affect the products of a coke-oven battery. Slowing down the coking rate produces coke of large size, more silvery in appearance and often stronger, the gas and by-products contain more low-temperature constituents; the light oil is higher in paraffins; there is a bigger yield of tar high in tar acids; there is less naphthalene and the light oil contains more toluene, xylene and solvents, at fast coking rates these are partly replaced by benzene. The influence of changes in the coking rate from full capacity down to only 20% of capacity on the operating costs, by-product costs and overhead costs is shown in three sets of curves.

**Carbon Deposition in Coke-Oven Roofs.** G. E. Foxwell. (Coke and Smokeless-Fuel Age, 1942, vol. 4, July, pp. 151-153). The author discusses possible causes and methods of preventing the deposition of carbon in coke-oven roofs. The thermal decomposition of gases has always been the most important source of carbon deposition. Methane is one of the most difficult gases to decompose into its elements; at 600-800° C. the decomposition is very slow, but after some carbon has been deposited this appears to act as a catalyst and accelerate the decomposition. Where iron spots are present in bricks the iron also acts as a catalyst, and the carbon grows in these regions, with ultimate failure of the brick. The temperature of the free space in the coke-oven is a critical factor,

and temperature control of this space may well be at the root of successful coke-oven design and operation. To eliminate carbon troubles the general principle suggested is that of endeavouring to secure the optimum conditions for benzole production. It happens, fortunately, that the best conditions for benzole production include a reasonable temperature in the free space, and this is just below the temperature at which carbon deposition becomes appreciable.

**Physical Properties of Cokes from Bureau of Mines-American Gas Association Tests at 800° and 900° C.** D. A. Reynolds and C. R. Holmes. (United States Bureau of Mines, June, 1942, Report of Investigations No. 3650). The authors report the results of BM-AGA (Bureau of Mines-American Gas Association) carbonisation tests on a number of American coals and blends, showing in particular the average physical properties of coke made in 13-in. and 18-in. retorts.

## PRODUCTION OF IRON

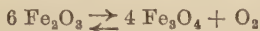
(Continued from pp. 166 A-167 A)

**Standardisation of Hot-Blast Valves and Hot-Blast Mains.** A. Rein. (Stahl und Eisen, 1942, vol. 62, July 16, pp. 601-605). The author discusses the design of hot-blast mains and valves with a view to reducing the number of types and patterns necessary for making them. A number of designs are illustrated and a table of proposed standard dimensions covering the range from 800 mm. to 2000 mm. inside dia. is presented. The refractory linings are also dealt with.

**New Developments in Blast-Furnace Charging.** A. J. Whitcomb. (Iron and Steel Engineer, 1942, vol. 19, June, pp. 29-48). The author gives a very detailed account of recent developments in the control of blast-furnace charging equipment. The reasons for the adoption of pneumatic bell-hoist mechanism are given, as well as details of electrical control for timing the openings of the small and large bells with the ascent and tipping of the skips of ore, coke and limestone and the movements of the revolving distributor. Descriptions are given of an automatic measuring device for the coke volume, a stock watering device, an automatic stockline recorder, and finally of a master control panel for controlling the distribution of the charge on the large bell, and the loading of the skips. This panel is fitted with signal lights indicating the movement of skips, what they contain, how many skip-charges are already on the large bell, the positions of both bells, the angle through which the distributor will rotate between successive skip-charges and the level of the stock in the furnace.

**The Behaviour of Iron Oxide with Some Admixed Foreign Oxides at Temperatures of about 1300° C.** N. G. Schmah. (Zeitschrift

für Elektrochemie und angewandte physikalische Chemie, 1941, vol. 47, Dec., pp. 835-843). The author studied the effect of the presence of  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  on the equilibrium



by direct isothermal measurement of the oxygen pressures prevailing in the systems. The temperature chosen for the experiments was as a rule  $1323^\circ \text{C}$ ., in some cases  $1060^\circ \text{C}$ . The results, which are represented as isothermal concentration-pressure diagrams, led to the following conclusions: (1)  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  affect the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  system relatively little.  $\text{BeO}$  does not form a spinel with  $\text{Fe}_2\text{O}_3$ , but adsorbs some  $\text{Fe}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  forms to some extent a solid solution with  $\text{Fe}_2\text{O}_3$ , but formation of the compound  $\text{FeO}.\text{Al}_2\text{O}_3$  could not be established. The presence of  $\text{SiO}_2$  did not lead to silicate formation. (2)  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  greatly affect the equilibrium by the formation of very stable solid solutions. The formation of ferric titanates was observed. (3) The presence of  $\text{Mn}_2\text{O}_3$  leads to the formation of the spinel  $\text{MnO}.\text{Fe}_2\text{O}_3$ .

**The Recovery of Iodine and Potassium Chloride from Blast-Furnace Flue Dust.** P. Dickens and W. Middel. (Stahl und Eisen, 1942, vol. 62, June 18, pp. 518-525). It has been found that in German blast-furnace practice the iodine content of the blast-furnace flue dust varies between 0.001% and 0.2%. In the present paper the authors describe a process for the recovery of iodine and potassium chloride from the dust collected from dry electrostatic blast-furnace-gas cleaners. A procedure for determining the amount of iodine present is first described. The iodine is present in a water-soluble form, but when it is leached out with water, potassium and sodium salts and some organic compounds are also dissolved. The interference of the organic salts can be overcome by giving the residue obtained on vaporising the liquor a heat treatment under oxidising conditions. A process was worked out by which the fluorine was separated from the potassium chloride and 70% of all the potassium salts present in the blast-furnace flue dust was recovered as 98.5%-pure potassium chloride.

**The Applicability of Blast-Furnace Slag in the Cement Industry.** R. Grün. (Iron and Steel Institute, 1942, Translation Series, No. 111). An English translation is presented of a paper which appeared in Stahl und Eisen, 1942, vol. 62, Apr. 9, pp. 301-307). (See p. 46 A).

**Electrothermal Ferro-Alloy Production in Brazil.** W. A. Darrah. (Electrochemical Society, Apr., 1942, Preprint No. 81-29). The author presents a brief report on the availability in Brazil of raw materials for making ferro-silicon, ferro-manganese, ferro-chromium and ferro-tungsten and on the electric power which would be required to produce these materials, and makes suggestions as to the design of suitable plants for immediate erection and post-war requirements.



**Contribution on the Production of Iron by Reduction with Hydrogen.** M. A. Kassem. (Eidgenössische Technische Hochschule in Zürich, 1942). After surveying the history of various direct methods of producing iron and briefly describing the more important ones, such as the Krupp-Renn process, the author discusses the suitability of hydrogen as a reducing agent for iron ore. A comparison of its properties with those of reducing gases containing carbon demonstrated the superiority of hydrogen for this purpose. He discusses the effects of temperature and pressure on the rate of reduction with hydrogen, and describes laboratory experiments on the direct reduction of ferric oxide and ferrous sulphide with hydrogen which led to the following conclusions: (1) It is practically impossible to achieve 100% reduction; (2) a high degree of reduction of ferric oxide can be attained at 500° C., which is a considerably lower temperature than that established by other investigators; (3) ferric oxide is much more easily reduced than iron sulphide; (4) it is probable that a process of autocatalysis takes place and assists the reduction of ferric oxide; (5) there is no evidence of autocatalysis in the reduction of iron sulphide; (6) not only the chemical composition, but also the physical and crystallographic properties have an important bearing on the reduction of iron ore.

**Powder Metallurgy in the Production of Iron Oil Pump Gears.** (Machinery, 1942, vol. 61, Aug. 20, pp. 203-206). A description is given of the process of making oil pump-gears from a mixture of iron particles and graphite by the powder-metallurgy process. The properties of the finished gears are also discussed.

## FOUNDRY PRACTICE

(Continued from pp. 167 A-168 A)

**Blast Control in the Foundry Cupola.** S. A. Herres and C. H. Lorig. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 67, Aug. 6, pp. 323-327). The authors discuss measures which can be taken to obtain proper control of the cupola blast with a view to ensuring a constant ratio of oxygen in the blast to carbon in the coke. They present two nomograms and a chart. The first enables a rapid determination to be made of the percentage variation from the normal blast volume for any combination of thermometer and barometer readings; the second simplifies the determination of humidity for blast calculations; and the third shows the weight of coke required per hour for different volumes of blast per minute over a wide humidity range. Some examples of the application of these diagrams are given.

**The Metallurgical Possibilities when Melting Cast Iron in the Cupola.** H. Kopp. (Giesserei, 1942, vol. 29, July 10, pp. 237-243). The author considers the cupola process not merely as one for remelting iron, but as a process to which methods of control can be applied with the object of imparting certain properties to the iron

produced from it. He divides melting practices into the following groups : (1) When it is desired to produce an iron of medium quality without purposely altering the properties of the iron charged ; (2) when a low-carbon, high-strength iron is required ; and (3) when a fluid iron with more than the usual carbon content is required. These processes and methods of modifying them are discussed in turn. In testing the effects of adding silicon in the form of 10% ferro-silicon and as silicon briquettes, it was observed with the former that the carbon content of the iron had dropped by more than the amount expected ; this difference varied with the amount of silicon introduced. But when briquettes were used, this extra reduction of the carbon content was not observed, the reason being that the carbon content of the melt had had time to reach its ultimate level before the silicon was dissolved out of the briquettes.

**Molten Metal Conditions Affect Casting Quality.** F. G. Sefing. (Foundry, 1942, vol. 70, July, pp. 78-79, 163-167). The author describes the conditions which adversely affect the production of sound iron and steel castings and discusses what measures can be taken to minimise these effects. He deals in particular with assisting the removal of gases from the molten metal and maintaining proper pouring temperatures. The optimum melting temperature range for grey iron is 2700-2900° F., the lower figure being high enough for heavy castings provided that the pouring temperature does not fall below 2600° F. A melting temperature exceeding 2900° F. tends to produce a fine dendritic graphite structure in the solidified iron which lowers the mechanical properties.

**A Critical Survey of Present-Day Methods in the Manufacture of Very Hard Chilled Rolls.** Atkin. (Proceedings of the Cleveland Institution of Engineers, 1940-41, No. 6, pp. 119-138). The author surveys methods of casting very hard chilled rolls with special reference to composite rolls. An early method was to pre-cast the shell and use this as an insert in the mould into which the core-iron was poured, but this has been superseded by a process in which the mould is first filled, or almost filled, with a hard alloy iron and, after allowing time for the outside to solidify, displacing the core-metal with a softer and tougher iron ; three ways of doing this are in vogue to-day. In the first the flow of the two kinds of iron is in the same direction ; in the second method (due to Gontermann and Peipers) the soft metal is poured into the mould through the feeder-head, and the hard metal is forced back up the down-gate through a valve, and when it is judged that all the hard metal has been displaced, the valve is closed and the roll is filled up to the top of the feeder-head. The third method is a modification of the first in which an outlet gutter for the hard metal is provided at the top neck. The advantages and disadvantages of these methods are pointed out.

**The Production in Rotary Furnaces of Steel for Castings.** F. A. Lemon and H. O'Neill. (Iron and Steel Institute, 1942, this Journal, Section I.). The manufacture of plain carbon steel in 5-ton

Sesci rotary furnaces is described. The furnaces use monolithic acid refractory linings of British origin, and are fired with pulverised coal. The charge consists of 98.5% of railway spring and tyre scrap with not more than 1.5% of pig iron. After numerous experiments the procedure is now to boil, work down and finish in a normal way, though ore additions are seldom required. Details are given of the properties of the resulting steel and slag, and the working data are compared with those of a 35-ton fixed acid furnace.

Great difficulties were encountered in securing a good life from the refractory linings. With intermittent working this has been raised from a beginning of 29 heats per lining to an average of 125, with a record value of 226. In Appendix A, T. Fletcher describes a daily patching technique, developed to enable improved life to be obtained, and in Appendix B, J. N. Bradley presents chemical, physical and petrographical data of patch and various lining materials. It has been found that the most useful lining is one with adequate refractoriness and low after-expansion, but, above all, a facility for forming a durable ceramic bond with the patch repair.

**Casts Steel Anchors Vertically.** W. Bell, jun. (Foundry, 1942, vol. 70, July, pp. 69, 161, 162). A brief description is given of the procedure for moulding, casting and heat-treating cast-steel anchors at a Canadian foundry. The mould is made flat in a two-part flask which is turned on end before pouring and two 14-in.-dia. risers are provided.

**Effect of Material, Shape and Moulding Technique on the Efficiency of the Steel Foundry.** H. Resow. (Iron and Steel Institute, 1942, Translation Series, No. 104). An English translation is presented of a paper which appeared in *Giesserei*, 1938, vol. 25, Sept. 9, pp. 447-450. (See Journ. I. and S.I., 1938, No. II., p. 347 A).

**Practical Economics in the Use of Corebinders.** A. Tipper. (Institute of British Foundrymen: Foundry Trade Journal, 1942, vol. 68, Sept. 10, pp. 27-31; Sept. 24, pp. 71-76). The author surveys the materials used for making cores and suggests methods of using them with the greatest efficiency so as to reduce the consumption by foundries of the vegetable, marine and fish oils and other imported products. The factors to which particular attention is drawn include good mixing, use of the cleanest and most uniform sand, the adoption of regular and controlled baking conditions to suit the particular binders used, good storage conditions for the cores and regular testing to ensure the uniformity of the raw materials.

**Handling Castings Through the Cleaning Room.** J. M. Munroe. (Foundry, 1942, vol. 70, July, pp. 70, 171). The author gives a brief illustrated description of the improved system installed at an American foundry for handling large numbers of small castings. A motor carrier with a lifting device on the front is used to pick up and transport corrugated steel boxes into which the castings are piled.

**Molding Large Iron Castings.** P. Dwyer. (Foundry, 1942, vol. 70, July, pp. 72-74, 147-149). The author describes and illustrates the moulding operations at an American foundry where large iron castings weighing up to about 40 tons are produced.



**Moulding a Cast-Iron Base.** W. Gudgeon. (Foundry Trade Journal, 1942, vol. 68, Sept. 24, p. 81). The author describes the preparation of the mould and core for an iron casting of unusual shape. This casting consisted of a top frame 3 ft. 9 in. square with a taper pipe 19. in. long with a diameter of 2 ft. in the plane of the frame, the whole casting weighing 6 cwt.

**The Solidification of Steel Castings.** D. W. Rudorff. (Metallurgia, 1942, vol. 26, July, pp. 99-102). An abridged English translation is presented of a paper by N. Chworinoff in which laws governing the solidification of steel castings are developed from thermal-conductivity data. (See Journ. I. and S.I., 1941, No. II., p. 116 A).

## PRODUCTION OF STEEL

(Continued from pp. 169 A-172 A)

**Copperweld Steel Company.** T. J. Ess. (Iron and Steel Engineer, 1942, vol. 19, May, pp. 35-41). The author gives an illustrated description of the new steel works of the Copperweld Steel Co., in eastern Ohio, which commenced operations in 1939. Steel is produced in six large electric-arc furnaces, four of which are top-charged, the roofs being lifted and swung by hydraulic rams. The charging time is about 10 min.; the total time of heat, tap to tap, is  $7\frac{1}{2}$ - $8\frac{1}{2}$  hr. for the larger furnaces (40-50 tons each) and  $6\frac{1}{2}$ - $7\frac{1}{2}$  hr. for the smaller furnaces (10 tons each). The ingot stripper is of unusual design, in that the stripping is done in the horizontal position and the ingots are pushed out on to a bogie. Some particulars of the rolling-mill and finishing department are also given.

**A Hundred Years of Steel Progress.** (British Steelmaker, 1942, vol. 8, Aug., pp. 179-186). A brief account is given of the origin, development and present plant of Samuel Fox and Co., Ltd., Stocksbridge. In 1842 Samuel Fox commenced the manufacture of wire for textile pins; in 1854 he produced cold-rolled steel strip and in 1860 he installed 48 melting holes to produce his own raw material, *i.e.*, 1500 tons of crucible steel per annum. The present limited company was formed in 1871, and the plant now includes electric furnaces, railway tyre mills and mills for rolling high-quality steel strip, stainless-steel strip, and strip for galvanising and lacquering.

**Jet Distribution on Converter Bottoms.** H. Schwiedessen. (Iron and Coal Trades Review, 1942, vol. 145, Aug. 28, pp. 701-702). An abridged English translation is presented of a paper which appeared in Stahl und Eisen, 1942, vol. 62, Mar. 26, pp. 269-270, in which the author shows how to calculate the number, diameter and form of distribution of the blast-holes in the bottom of a Bessemer converter. (See p. 50 A).

**Significance of the Bessemer End-Point.** H. T. Bowman. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1428: Metals Technology, 1942, vol. 9, Feb.).



The author discusses how the length of the after-blow, the metal temperature and the number of blanked-off tuyeres in Bessemer converter practice affects the quality of the steel. The more tuyeres there are blanked-off the less oxidation takes place during the after-blow, consequently there will be less  $\text{FeO}$  in the steel. The length of the silicon-elimination period as shown by photo-electric cell records of the flame intensity is an accurate indication of the amount of silicon in the metal being blown. The higher the temperature of the metal the higher is the solubility of iron oxide in it. If the converter is turned down before the flame-drop, the slag will be dry and coarse in appearance; as the after-blow is extended, the slag becomes "wet" and more liquid; with severe overblowing it is difficult to prevent the slag from running into the ladle with the metal.

**Control of the Basic Bessemer Process by Measurement of the Radiation of the Converter Flame.** G. Naeser and H. Krächter. (Iron and Steel Institute, 1942, Translation Series, No. 105). This is an English translation of a paper which appeared in *Stahl und Eisen*, 1942, vol. 62, Apr. 23, pp. 341-347. (See p. 103 A).

**Proceedings of the Twenty-Fifth Open-Hearth Conference.** (American Institute of Mining and Metallurgical Engineers, Open-Hearth Conference, Apr. 16-17, 1942). The Twenty-Fifth Open-Hearth Conference of the American Institute of Mining and Metallurgical Engineers was held at Cincinnati, with L. F. Reinartz as the General Chairman. Separate sessions on basic and acid open-hearth practice and one joint session were held.

The first paper of the basic open-hearth session was presented by C. R. Hook; this dealt in a general way with attaining maximum efficiency of steelworks production in war-time, and amounted to an appeal for more co-operation between management and men. This was followed by the paper which gained the McKune Award, in which H. B. Emerick and S. Feigenbaum discussed the duplex process (see p. 137 A). J. T. Bauer then read a paper in which the reactions governing the formation and control of the slag in basic open-hearth furnace operation were explained in a manner suitable to be a guide to the first helper; in an appendix the procedure for slag sampling and examination was described. The desirable properties of iron ores for the basic open-hearth process using charges with a high proportion of hot metal and a minimum of steel scrap was discussed in R. W. Tindula's paper; he observed that with magnetite ores a coarse sinter gave much better results than medium and fine concentrates, but with hematite ores there was little difference in the results obtained with coarse and fine ores; most heats were charged with fine hematite ores first, and then about half as much sinter was added to cover this. In the next paper J. S. Morris outlined a programme for the training of open-hearth personnel. A brief discussion then took place, in which experiences were interchanged on the life of open-furnace bottoms rammed with "Ramix" and "Plastic KN"; as a contribution to this H. N. Barrett, jun., read a paper entitled "Applications of Magnesitic Ramming

Mixtures," in which the ramming of a 175-ton open-hearth furnace with "Ramix" was described in detail with numerous illustrations. He was followed by I. A. Nicholas, who discussed bottoms for basic open-hearth furnaces and gave details of the composition and properties of "StaSet" and "StaSet Special C," the former containing 70% of magnesia and 14% of lime, whereas the latter is a mixture of "StaSet" and chrome ore. F. L. Toy discussed means of improving the plasticity of Californian and Cuban chrome ores; for Californian chrome ore he suggested fine-grinding and the addition of 10% of Washington magnesite. Open discussions on increasing the speed of furnace repairs, temporary roof-patches, suspended roof construction, monolithic rammed doors, the supply of magnesite, chrome ore, and graphite, and ladle-nozzles then took place. In the latter part of this discussion reference was made to the use in ladles of a large nozzle-cap brick weighing 63 lb., into which the nozzle is set with a thin fireclay slurry; there is a saucer-shaped well in the cap-brick, and this prevents the formation of skull. The cap-brick usually lasts as long as the ladle lining, and a clean shut-off is obtained during the entire pour. In a discussion on the pig-ore process, J. J. Golden reported that from an analysis of process data on several thousand heats it was found that the optimum percentage of carbon in the steel at "melt-down" in relation to the rate of production was at 0.35-0.50% above the carbon content desired at tapping. T. S. Washburn pointed out that, up to about 75% of hot metal, increasing the proportion of hot metal in the charge decreased the time from charging to "melt-down," but above this point there was a sharp increase in the melting time, owing to the reduced efficiency of the charged ore; he illustrated the effect of ore additions on the rate of carbon drop with several curves. J. A. Sample reported on the advantages of installing a spectrograph at a steelworks laboratory for making rapid determinations of copper and tin in heats containing large proportions of scrap. T. L. Toy and W. O. Philbrook each made contributions on the use of the photo-electric colorimeter (or photometer) for making rapid determinations of nickel, chromium, molybdenum, nitrogen, phosphorus and silicon; this instrument offers a means of measuring quantitatively the transmission of light by a solution. W. O. Philbrook also reported on experience with the Leco apparatus for making carbon and sulphur determinations. J. Chipman presented and discussed the results of some laboratory work on the carbon-oxygen equilibrium in liquid iron at pressures up to 300 lb. per sq. in. From these he concluded that the oxygen in the metal was not all present as  $\text{FeO}$ , but partly as  $\text{CO}$ , and from the data he estimated the solubility of carbon monoxide in liquid steel at 1 atm. to be 0.002-0.004%; he also found that there was more than the equilibrium content of oxygen in the bath during the finishing period of an open-hearth heat. Several delegates then spoke on experience gained in attempts to reduce the consumption of manganese and aluminium. C. E. Sims referred to additions of

very small amounts of aluminium to killed steels, pointing out that unless sufficient was added to leave a slight excess, no efficient deoxidation is obtained; additions of, say, 3-8 oz. per ton of killed steel were useless, and should be discontinued. The effect of tin arising from charging compressed cans on the rolling properties of steel was discussed next. R. D. Hindson stated that a 100-ton heat of steel high in sulphur, with 0.08% of carbon and as much as 0.215% of tin rolled very well, and he was considering the theory that tin had least effect on high-sulphur steel. V. W. Jones referred to a mill for removing enamel from scrap enamelled sheets. A paper on recovering steel from steelmaking slag was then read by F. E. Ullman (*see* p. 169 A). The first day's basic open-hearth sessions concluded with a discussion on the manufacture of high-sulphur shell steel.

On the second day J. D. Gold and S. M. Newbrander gave an account of the use of blown metal for making basic open-hearth steel at the Weirton Steel Company's works. C. H. Herty, jun., then reported on an investigation of the use of soft ore in the open-hearth; generally speaking, an ore with less than 3% ignition loss and less than 7% of silica can be used alone when the charge consists of up to about 61% of hot metal. An account of open-hearth practice in Australia, where 80% of hot metal is normally charged, was given by L. B. Lindemuth. The briquetting of soft ore to facilitate drying it was described by V. W. Jones. The next contribution was by J. E. Greenawalt on methods of producing open-hearth sinter; he thought that the sinter of the future would be made from fine ores low in silica, sintered with enough limestone to flux the silica in it, and charged under conditions calculated to produce the maximum amount of FeO. W. C. Buell, jun., then compared English and American mixer practice, giving data on the cost of production.

On the second afternoon of the Conference a joint session on basic and acid open-hearth operation was held. M. F. Yarotsky and E. J. Dattisman, jun., each spoke on procedure adopted at their respective works to obtain closer co-ordination between the open-hearth and rolling-mill departments. P. M. Reinartz explained the U.S. Government's new steel expansion programme. W. W. Bergmann described an improved type of ingot mould stool (*see* p. 56 A). J. A. Clauss read a paper describing the fuel-oil supply system of the Great Lakes Steel Corporation, and J. R. Green described the Brown system of fuel-rate control for regenerative furnaces.

In the separate session on acid open-hearth practice open discussion took place on: (a) Charging practice with special reference to the use of light scrap; (b) the limits within which the carbon can be controlled in melting down; (c) methods of slag control; (d) melting practice; and (e) finishing practice. G. R. Fitterer then presented a paper entitled "Gases in Acid Open-Hearth Steel," in which he dealt mainly with factors favouring the absorption of nitrogen. Open discussion was then continued on ladle practice,



pouring practice, factors affecting the surface of steel castings and repairing furnace bottoms after tapping.

**Process Results with an Open-Hearth Furnace Fired with Coke-Oven Gas (Cold-Gas Practice).** E. Gnida. (Stahl und Eisen, 1942, vol. 62, July 16, pp. 612-614). The author presents and discusses statistics of the first campaign (1012 heats) of a 50-ton coke-oven-gas-fired open-hearth furnace installed in 1940 to replace a producer-gas-fired furnace at one of the works of the Röchling combine.

**The Manufacture of High-Quality Low-Cost Steel.** P. J. McKimm. (Steel, 1942, vol. 111, July 13, pp. 90-92, 120-122). Continuation of a series of articles (*see* p. 103 A). The author discusses the production during pouring operations of scrap for remelting, the use of two-nozzle ladles and the treatment of ingot moulds. Remelting scrap has been produced in the slag thimble by filling the bottom with sponge iron and permitting the slag from the steel ladle to overflow into the thimble. In American practice ingot-mould washes usually consist of a mixture of aluminium-bronze powder and graphite in a liquid vehicle, such as molasses diluted with water. From the point of view of steel quality, rimming steel should be held in the ingot mould for about 1 hr. before stripping; a 2-hr. period is recommended for killed steels.

**The Electric-Arc Furnace.** T. F. Wall. (Engineer, 1942, vol. 174, Aug. 28, pp. 175-177; Sept. 4, pp. 188-191; Sept. 11, pp. 216-218; Sept. 18, pp. 228-230). After briefly describing the work of Siemens, Stassano and Héroult in developing the electric-arc furnace for metallurgical purposes, the author discusses in detail the characteristics of the electric-arc and modern carbon-arc furnaces in the iron and steel industry, with special reference to the transformers and choking coils used, the properties of electrodes, systems of electrode regulation and skin effects in the leads of an electric arc furnace.

**Insert Triples Life of Mold Stools.** (Steel, 1942, vol. 110, May 4, pp. 82-85, 110). A brief description is given of an ingot-mould stool of special design which increases its life. This stool consists of a cast-steel frame into which is cast an iron centre or insert. The iron resists the heat of the molten steel, and the steel frame resists the stresses set up by the heat. This mould stool has been found to last three times as long as an all-iron stool of the standard type.

**High Speed Steel.** H. W. Pinder. (Iron Age, 1941, vol. 147, Mar. 27, pp. 39-43; Apr. 3, pp. 40-42). The author discusses factors affecting the heterogeneity of 4-in., 6-in. and 8-in square ingots of high-speed tool steel. The distribution of carbides after forging various portions of the ingots down to  $1\frac{3}{4}$ -in.-square bars was studied under the microscope. It was found that: (1) In all ingot sizes the best distribution was obtained in the bottom third of the ingot; (2) provided that the normal amount was cropped off, the next best position was the top third of the ingot; (3) despite an insufficient reduction in area, the 4-in.-square ingot had the best distribution of the three sizes, and this was confirmed by examining



specimens from bars made by further reduction of the  $1\frac{3}{4}$ -in squares to 1-in. rounds; and (4) to make special tools it is worth selecting steel originating from that portion of ingot with the best carbide distribution. The causes of failure of high-speed steel tools are dealt with and it is shown that defects which are detected after heat treatment or only after grinding may originate at earlier stages in the making of the tool. The magnetic-powder method of crack detection is suggested as a means of examining tools before heat-treating them.

**An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process.** D. Binnie. (Iron and Steel Institute, 1942, this Journal, Section I.). The manufacture and analysis of a rimmed-steel ingot are recorded. The examination included sulphur-printing of the longitudinal section of the ingot, chemical analysis throughout this section, and also micrographs of the zones which are particularly rich in sulphur. Attention was specially directed to the relationship of the carbon content of the core to the pit carbon value. In the ingot submitted the general analysis of the carbon in the core was lower than the pit analysis. A survey of the rimmed-steel ingots published by the Committee on the Heterogeneity of Steel Ingots showed that the general analysis of the carbon in the core may be lower or higher than the recorded pit carbon content. An explanation of this phenomenon is derived from the balanced-composition hypothesis of Hultgren and Phragmén, which hypothesis has been developed mathematically to include the influence of manganese and pressure on the carbon and oxygen values of the balanced composition, and shows that, with increasing manganese content as well as with increasing pressure, the carbon content of the balanced composition is progressively increased. The importance of ensuring that a pit sample is fully representative of the ladle analysis is stressed.

**Rimming Steel.—Comparative Study of Three Ingots Received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France.** J. Mitchell. (Iron and Steel Institute, 1942, this Journal, Section I.). The analytical results obtained on two low-carbon basic Bessemer steel ingots are tabulated and compared with similar results obtained on earlier samples reported upon by the Committee on the Heterogeneity of Steel Ingots. The figures include variations in analysis found in the rim and core, and these are discussed from the standpoint of the light which they throw on the practical aspect of the rimming process.

**Defects.** J. Thomson and G. Campbell. (Journal of the West of Scotland Iron and Steel Institute, 1941-42, vol. 49, Part V., pp. 79-87). The authors indicate the types of defects which occur in steel, their characteristics and, where possible, methods of eliminating them. Most of the types described are those occurring in ingots, *e.g.*, piping, porosity, blowholes, skull and corner weakness, but cracks resulting from heat treatment and from forging at too low a temperature are also dealt with.

## REHEATING FURNACES

(Continued from p. 105 A)

**Bloom and Billet Heating Furnaces.** M. H. Mawhinney. (Iron and Steel Engineer, 1942, vol. 19, May, pp. 70-75). The author discusses developments in the design of new reheating furnaces and improvements to existing furnaces. The capacity of a batch-type billet furnace is determined by the hearth area, the usual rate of production being 20-35 lb. of steel per sq. ft. of hearth per hr., which is an average figure based on the production for a month. The lower limit of 20 lb. per hr. applies to small billets, and the upper limit of 35 lb. to large blooms where fast heating is permissible. Existing furnaces often have one or more of the following faults: (1) Regenerative firing which is difficult to operate with controlled atmosphere unless forced draft is applied; (2) stacks which create excessive draft; (3) insufficient insulation; (4) no provision for controlling temperature, fuel/air ratio and pressure; (5) excessive maintenance cost often due to poor design of doors and door frames; and (6) loss of time because of inadequate handling equipment. With continuous furnaces end-discharging by gravity, which is attractive because of simplicity, should be avoided when it is desired to maintain control of the atmosphere, since too much air gets in at hearth level. Instead there should be side discharge with a machine operating through the floor, or with a discharge pusher. In conclusion one or two billet manipulators are described and illustrated.

**Resistance Heating for Forging.** A. F. Macconochie. (Steel, 1942, vol. 110, June 15, pp. 64, 72). The author compares the thermal efficiencies of fuel-fired furnaces and of internal electric resistance methods of heating, and describes and illustrates equipment for the internal resistance heating of 6-ft. bars and rivets; this method of heating has the advantage of light scale, accuracy of temperature control and increased comfort to the operator. Its disadvantages include wear of the electrode parts and trouble with the contacts.

## FORGING, STAMPING AND DRAWING

(Continued from pp. 172 A-173 A)

**Heavy-Duty Toggle-Actuated Press.** (Engineering, 1942, vol. 154, Sept. 11, p. 207). A brief illustrated description is given of a heavy-duty triple-toggle press which can exert a pressure of 500 tons and has a bottom platen with a surface measuring 5 ft. by 4 ft.

**Stainless Steel—Deep Drawing and Spinning Technique at the Lalance & Grosjean Mfg. Co. Plant.** H. Chase. (Iron Age, 1940,

vol. 146, Nov. 21, pp. 47-53). The author gives an illustrated description of the pressing, spinning and heat-treatment plant at the works of Lalance & Grosjean Manufacturing Co., Woodhaven, New York State. At this works stainless steel blanks No. 11 gauge,  $53\frac{1}{2}$  in. in dia., can be drawn into cylindrical shells 32 in. in dia., 18 in. deep.

**Patenting Steel Wire in Salt Baths.** E. Jaenichen. (Stahl und Eisen, 1942, vol. 62, July, 30, pp. 641-649). Attempts have been made in Germany to find a substitute for the lead bath for the patenting of steel wire and trials with molten salt baths have been conducted. In the present paper the author reviews previous investigations of the use of molten salts, discusses the availability of the salts, the design of plant and suitable material for the container. He finds that molten sodium nitrate with a specific gravity of 2.26 is quite satisfactory for patenting steel wire of the usual diameters, strengths and qualities, and that in certain respects it offers some advantages over lead-bath patenting.

## ROLLING-MILL PRACTICE

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(Continued from pp. 141 A-142 A)

**Grounded D-C Systems for Steel Mills.** L. L. Fountain and H. A. Travers. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 68-71). The authors discuss the advantages and disadvantages of operating a direct-current system for a rolling mill with one polarity deliberately earthed, or with both polarities unearthed.

**Report of Field Tests on I.R. Drop Compensation.** G. E. Stoltz. (Iron and Steel Engineer, 1942, vol. 19, May, pp. 51-58). The author studies the problem of controlling the speeds of motors driving the stands in a high-speed tandem strip mill. He presents several series of curves showing the speed fluctuations during the threading of a mill when the motor equipment includes compensation devices for the *I.R.* (current  $\times$  resistance) drop.

**Nonmetallic Bearings for Steel-Mill Service.** F. W. Vogt. (Steel, 1942, vol. 111, July 20, pp. 78-80). The author describes and illustrates some applications of synthetic-resin bearings to rolling mills, and gives a list showing that the reduction in the power consumption of different types of mill stands fitted with these bearings may vary from 10% to as much as 30%.

**Design of Lubricants for Mechanized Lubrication.** F. E. Rosenstiehl. (Iron and Steel Engineer, 1942, vol. 19, Mar., pp. 83-87). The author describes how lubricating oils are developed which have a high load-carrying capacity, and the tests for determining the resistance of an oil to oxidation and emulsification.

**Oil Filtration and Reclamation.** C. A. Bailey. (Iron and Steel Engineer, 1942, vol. 19, May, pp. 61-67). The author describes the

essential features of small and large oil-circulating systems and discusses mechanical and chemical methods of reclaiming used oil. Some methods of testing filters, and the acidity and amount of sediment in oils are described first, and details are then given of a large circulating system suitable for a five-stand, four-high, tandem strip mill. For the reclamation of used oils in a rolling mill the important item of the equipment is a centrifuge, either portable or stationary, which should be in a room with sufficient storage tanks and heating facilities for the types of oil to be treated; the arrangement should be flexible, so that a wide quantity range can be conveniently treated, *e.g.*, 50 gal. of one type of oil and 5000 gal. of another type. A classification system for reclaimed lubricants according to type with a symbol to represent each is suggested.

**The Planning and Designing of Wide Strip Mills.** (Metallurgia, 1942, vol. 26, July, pp. 96-99). Some of the principal factors which control the design of hot and cold strip mills are discussed; the information presented is based on two recent German reports by Timmermann and Lemm respectively (*see* pp. 14 A, 141 A and 59 A).

**Some Considerations in the Designs of Wide-Strip Mills.** H. P. Lemm. (Sheet Metal Industries, 1942, vol. 16, Aug., pp. 1137-1143; Sept., pp. 1316-1318). An abridged English translation is presented of a paper which appeared in *Stahl und Eisen*, 1942, vol. 62, Mar. 26, pp. 257-265 in which the performances of continuous and semi-continuous wide strip mills are compared (*see* p. 59 A).

**The Production of Seamless Vessels.** (Iron and Steel, 1942, vol. 15, Aug., pp. 423-424). A brief description is given of the Röckner process of rolling large seamless steel vessels up to 6 ft. in dia. and 60 ft. in length. This rolling process is carried out by radially arranged sets of rolls acting upon both the external and internal surfaces of the hollow body. Longitudinal movement of the piece through the mill is achieved by setting the roll axes obliquely to the longitudinal axis of the piece.

## HEAT TREATMENT

(Continued from pp. 173 A-174 A)

**Industrial Controlled Atmospheres.** N. K. Koebel. (Iron Age, 1940, vol. 146, Nov. 21, pp. 33-39; Nov. 28, pp. 40-46; Dec. 5, pp. 45-51; Dec. 12, pp. 48-53). The author describes methods of producing and controlling heat-treatment furnace atmospheres. The carburising power of an atmosphere may be determined by hardness tests, examining micrographs, analysing metal removed in consecutive cuts and by determining the gain in weight of the part after treatment; the advantages and limitations of these four methods of testing are pointed out, after which the author describes the theory and practice of heat treatment by: (a) heating in an



atmosphere produced by burning a controlled mixture of town gas and air; (b) pack hardening; (c) heating in carbonaceous muffle-blocks; and (d) heating in an atmosphere formed by cracking a liquid hydrocarbon. Turning to more recent improvements, the author deals next with the purification of atmospheres to remove carbon dioxide, sulphuretted hydrogen and moisture, giving a flow sheet of a plant for this purpose. The double cracking of town gas and natural gas is referred to. This consists first of cracking the methane component into hydrogen and carbon dioxide, and then causing these constituents to react with each other endothermically to produce water and carbon monoxide; the gas is finally passed through an activated alumina dryer to remove the moisture. Some installation and operating cost data for this double cracking plant are given. In conclusion, details of charcoal gas generators and test data on steels hardened in the various atmospheres described are presented.

**Drill Steel Sharpening Practice at Lake View and Star Gold Mine.** L. E. Elvey. (Proceedings of the Australasian Institute of Mining and Metallurgy, 1941, Dec. 31, No. 124, pp. 187-192). The author gives a detailed description of a drill-sharpening shop at an Australian gold mine. Low-pressure, end-fired furnaces were recently adopted in place of high-pressure furnaces, and this resulted in a greatly increased life of the furnace linings, with better control of the heat and better working conditions in the shop.

**Tool Steels.** D. Taylor. (Automobile Engineer, 1942, vol. 32, Sept., pp. 347-350). The author discusses factors influencing the selection of tool steels for various purposes and methods of heat treatment necessary to ensure optimum results. The minimum plant required to give complete scientific control of the heat-treatment operations is described.

**Heat Treatment with Salt Baths.** L. E. Raymond. (Iron Age, 1941, vol. 147, Apr. 3, pp. 31-34; Apr. 10, pp. 52-56; Apr. 17, pp. 32-34). The author presents and discusses data on the case-hardening of steel in salt baths. Erratic results were obtained using baths with the NaCN content controlled at between 30% and 40%; this was due to the presence of varying amounts of sodium cyanate. Carburising is less effective with about 1% of sodium cyanate present than with about 5%. At the lower case-hardening temperatures the nitrogen concentration is relatively high, and as the carburising temperatures are increased the carbon content of the case increases and the nitrogen content decreases. Coarse-grained steels carburise faster than fine-grained steels. Descriptions of salt-bath hardening procedure and plant are given.

**Precise Heat Treating Enables Carbon Steel Parts to Meet Critical Machine Tool Requirements.** F. W. Curtis. (Steel, 1942, vol. 110, Aug. 3, pp. 73-76, 112, 113). The author describes the introduction of the induction-hardening system at a works making milling machines and oscillating grinders. It has been successfully applied

to the hardening of gears, and in several instances it has been found just as satisfactory to employ a 0.40% carbon steel as it was to use a case-hardened low-alloy steel. A number of operations can also be dispensed with when induction hardening is applied. For instance, after rough-cutting the teeth of a low-alloy steel gear it was then necessary to carburise, finish-cut, harden, temper, clean and lap; it is now necessary only to rough-cut and finish-cut the teeth and induction-harden. Illustrations of the induction-hardening equipment are presented.

**Practical Application of Flame Hardening.** A. L. Hartley. (*Mechanical Engineering*, 1942, vol. 67, July, pp. 531-540). The author describes methods of controlling flame-hardening and the equipment and procedure at the plant with which he is connected. There appears to be no method of determining the temperature of a part during the flame-hardening operation; reproducible results can, however, be obtained by controlling the following variables: (1) The characteristics of the equipment; (2) the oxygen and acetylene pressure; (3) the distance between the work face and the burner tip; (4) the time the flame impinges on the metal; and (5) the design of the parts to be hardened. The results obtained by controlling these factors can be interpreted by using the microscope. For this purpose it is necessary to have a standard set of specimens for each material to be flame-hardened; these can be prepared by furnace-hardening a series of small cubes of the given material from a wide range of known temperatures; they are carefully polished and used as standard structures for the known temperature from which they were quenched. By adjusting the above five variables the flame-hardening conditions can be established for producing a required hardness by comparing the microstructures obtained with those of the standard specimens. Two flame-hardening machines are described in detail with many illustrations; one is a machine for hardening gears up to 12 in. in dia. by the spinning method, and the other is a machine of special design capable of hardening machine-tool parts up to 18 ft. long and 34 in. wide.

**Flame-Hardening Cylindrical Surfaces.** S. Smith. (*American Welding Society: Steel*, 1942, vol. 111, July 20, pp. 76, 82, 97, 98; Aug. 3, pp. 92-95, 119). The author describes the equipment and technique for flame-hardening the surface of cylindrical bodies, and discusses factors affecting the selection of equipment suitable for different parts. It is better in most cases to keep the bar or tube in a horizontal position for flame-hardening, but for diameters above about 10 in. the vertical position facilitates the control of the quenching stream.

**Elimination of Oxide Films on Ferrous Materials by Heating in Vacuum.** V. C. F. Holm. (*Journal of Research of the National Bureau of Standards*, 1942, vol. 28, May, pp. 569-579). An investigation of the mechanism by which lightly oxidised specimens of ferrous materials were brightened when heated in a vacuum

showed that the presence of carbon was essential. Oxidised specimens of iron containing small amounts of carbon were brightened in 15 to 20 min. at 800° C., and the elimination of the oxide film was accompanied by a decrease in the carbon content. The removal of oxide films on stainless steel also took place when the specimens were heated to about 1050° C. Oxidised iron of high purity containing less than 0.001% of carbon could not be brightened by heating in a vacuum at temperatures up to 1250° C. Vacuum-heating of lightly oxidised specimens of high-purity iron sometimes caused the oxide film to agglomerate, forming distinct geometric patterns that could be observed under the microscope.

**The Scaling Resistance of Steels Alloyed with Vanadium.** H. Cornelius and W. Bungardt. (Iron and Steel Institute, 1942, Translation Series, No. 109). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Aug., pp. 107-113. (See p. 17 A).

**Effect of the Quenching Temperature when Hardening and Tempering Steel.** R. Schäfer and W. Drechsler. (Stahl und Eisen, 1942, vol. 62, June 11, pp. 497-503). The authors report on an investigation of the properties, after various forms of heat treatment, of the German case-hardening steels ECMo 100 and EC 100, the former containing carbon 0.20%, manganese 1.05%, chromium 1.12% and molybdenum 0.24%, and the latter carbon 0.23%, manganese 1.23%, chromium 1.51% and vanadium 0.14%, in order to ascertain whether the double hardening (*i.e.*, core-hardening and final hardening) could be successfully replaced by a more simple treatment. It was found that both very pearlitic and slightly pearlitic steels could be successfully hardened by cooling them slowly from the usual case-hardening temperature to the  $A_1$  point and then rapidly quenching. With this treatment there was no additional carbide precipitation with the very pearlitic steels, but with the slightly pearlitic steels there was some precipitation of ferrite at the grain boundaries; this, however, had no effect on the final hardness and mechanical properties. The precipitation of ferrite can be suppressed by the addition of vanadium or any other agent which strongly promotes carbide formation, and it is delayed by the addition of aluminium. If the specimens were slowly cooled to the  $Ar_3$  point, the ferrite precipitation was prevented and vanadium or aluminium additions were unnecessary.

## WELDING AND CUTTING

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(Continued from pp. 174 A-175 A)

**Electric Welding Machines.** C. J. Jennings and A. B. White. (Iron and Steel Engineer, 1942, vol. 19, June, pp. 50-60). The authors discuss and compare the characteristics of D.C. and A.C.

electric welding machines. The static volt-ampère curve of a welding machine cannot be used as the only guide to weldability; the dynamic characteristics must also be taken into account. A.C. machines of the transformer type have a higher electrical efficiency than rotating machines, but they have a poorer power factor unless power-factor correction is used. An A.C. transformer-type welding machine with proper power-factor correction is the most efficient type of single-operator welding equipment.

**Spot Welding of N-A-X High-Tensile Steel.** W. F. Hess and C. R. Schroder. (Welding Journal, 1942, vol. 21, May, pp. 241-S-244-S). The authors recently issued a report on the properties of spot welds in a low-alloy high-tensile steel sheet 0.040 in. thick known as "N-A-X High-Tensile Steel" (see p. 144 A). The present paper constitutes a supplementary report on spot welds in this material, the thickness this time being 0.070 in. The conclusions reached in the first report were confirmed.

**A Welding Flux for Sulphur Contaminated Steels.** I. Bencowitz. (Welding Journal, 1942, vol. 21, May, pp. 237-S-241-S). The author gives an account of tests made with a number of fluxes in order to determine a good mixture for making welds in steel in which unusually large amounts of sulphur are present. Bend and tensile tests were made on specimens, some of which were welded while molten sulphur was being poured over the joint. Various mixtures of manganese dioxide, borax, ground silica and other ingredients were tried, and, of these, the best results were obtained with one containing manganese dioxide 5 parts, borax 3 parts, ground silica 3 parts and kaolin 1 part.

**Corrosion Resistance of Welded Joints.** W. Spraragen and H. H. Chiswik. (Welding Journal, 1942, vol. 21, May, pp. 209-S-237-S). The authors review the literature from January 1937 to January 1941 on the corrosion resistance of welded joints in ferrous and non-ferrous metals.

## PROPERTIES AND TESTS

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(Continued from pp. 183 A-185 A)

**The Degree of Saturation as a Yard Stick for the Strength of Cast Iron.** A. Gimmy. (Giesserei, 1942, vol. 29, June 26, pp. 226-230). The author considers formulæ which have been proposed for estimating the properties of cast iron from the carbon and silicon contents. He presents tables showing the relation between the carbon and silicon contents, the degree of saturation and the tensile strength and explains why he prefers the factor  $C + 0.3 \text{ Si}$  to that



of Piwowarsky ( $C + \frac{1}{3} \text{Si}$ ). To calculate the degree of saturation he recommends the factor

$$\frac{C + \frac{1}{3} \text{Si}}{4} - 0.04$$

as one which gives a very accurate value.

**Carbon Steels.** J. W. Donaldson. (Metallurgia, 1942, vol. 26, July, pp. 94-95, 104). The author discusses the properties and applications of plain carbon steel with special reference to various specifications in the T.A.C. Schedules (Technical Advisory Committee of the Special and Alloy Steels Committee of the Ministry of Supply).

**The New NE (National Emergency) Alloy Steels.** (American Iron and Steel Institute : Steel, 1942, vol. 110, June 15, pp. 66-72). A further set of tables and curves showing the properties of heat-treated low-alloy steels is published (see p. 148 A). These steels are known in the United States as "National Emergency" steels, as they are intended to reduce the consumption of high-alloy steels.

**Properties of the New NE (National Emergency) Alloy Steels.** (American Iron and Steel Institute : Steel, 1942, vol. 111, July 13, pp. 80-86). An additional series of curves showing the hardenability and mechanical properties of the new "National Emergency" steels is presented. (See preceding abstract).

**National Emergency Steels NE 8600 to NE 8900.** J. H. Jones. (Metal Progress, 1942, vol. 41, June, pp. 793-799). In this paper the author reports the results of tensile, impact, hardness and hardenability tests on alloy steels made by one of the works contributing to an investigation organised by the Technical Advisory Committee to the War Production Board (U.S.A.). The steels tested all contained silicon 0.20-0.35%, nickel 0.40-0.60% and chromium 0.40-0.60%, with carbon and molybdenum rising from 0.18-0.23% and 0.15-0.25% to 0.45-0.52% and 0.30-0.40% respectively; the results are presented in numerous tables and graphs.

**New Steels Conserve Vital Alloying Elements.** (Machine Design, 1942, vol. 14, July, pp. 65-66). Tables of analyses with code letters and numbers of a new series of low alloy steels known as "National Emergency Steels" and lists of some possible alternative steels are presented. These have been prepared by the American Iron and Steel Institute and the Society of Automotive Engineers (see p. 148 A).

**NE (National Emergency) Alloy Steels.** C. M. Parker. (American Society for Testing Materials, 1942, vol. 110, Aug. 3, pp. 70, 71, 101, 102, 110, 111). The author describes how the National Emergency alloy steels were developed in the United States and discusses how the engineer can use the hardenability and composition data to predict some of the other properties, details of which are not yet available.

**The Technical Cohesive Strength and Yield Strength of Metals.** D. J. McAdam, jun. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1414: Metals Tech-

nology, 1942, vol. 9, Jan.). The author considers how the combination of the three principal stresses acting on a metal affects the technical cohesion limit and the yield stress, and presents evidence that these effects are not in accordance with prevalent views expressed in the literature. The technical cohesive strength of a metal cannot be represented by a single stress value, but comprises an infinite number of stress values corresponding to the infinite number of possible combinations of the principal stresses. Plastic deformation increases the technical cohesive strength continuously up to the point of fracture. The three-dimensional diagram representing the technical cohesive strength of a metal has a three-cornered contour; it lies in a plane perpendicular to the locus of polar-symmetric stresses, and tapers non-linearly to a point. The three-dimensional diagram representing the yield strength has a circular contour, and tapers non-linearly to the same point. For a ductile metal, the diagram representing yield strength is inside the other diagram. With plastic deformation the diagram representing yield strength is enlarged more rapidly than the technical-cohesive-strength diagram, and eventually the sides touch.

**Facts and Fallacies of Stress Determination.** J. O. Almen. (S.A.E. Journal, 1942, vol. 50, Feb., pp. 52-61). The author discusses methods of presenting fatigue-test data, and explains why results obtained on laboratory test specimens cannot always be applied to machined automobile parts. He concedes that the accuracy of stress data from photo-elastic and extensometer investigations is usually greater than that obtained from involved mathematical analysis, but, whilst two specimens of identical material and dimensions will show identical conditions of stress when studied by these two methods, they may vary widely in fatigue strength because of minute differences in surface finish. Several S/N curves (stress/number-of-cycles) are presented plotted with logarithmic scales for both ordinates and abscissae; these show that when the results of tests on a large number of commercially identical parts over a sufficiently large range of load are plotted, they lie within well-defined lines diverging from a point at a high stress value and low number of cycles in the direction of low stress and a high number of cycles. Two three-dimensional fatigue diagrams are presented and discussed. In these the vertical scale represents stress, the horizontal scale the number of cycles, and the depth scale the stress range from zero change in stress to a complete reversal.

**Glo-Crack.** (Engineer, 1942, vol. 174, Sept. 4, p. 201). A brief description is given of a new method of detecting cracks. The process depends on the fluorescence of certain materials when exposed to ultra-violet light. The specimen to be examined is immersed in a special bath of fluorescent material held at a temperature of 75° C. After a short time it is withdrawn and washed in a solution to remove all the fluorescent material from the surface. Should there be any crack in the surface, the fluorescent material

remains lodged in it, and, when the specimen is illuminated by ultra-violet light, any crack is shown up with startling vividness against a background of black or purple. The process will not reveal mere scratches with a depth equal to or less than their width.

**The Magnetic-Powder Method of Crack Detection.** J. F. Kayser. (Engineer, 1942, vol. 174, Sept. 18, p. 241). The author discusses the design of magnets used in the magnetic-powder method of crack detection. The cross section of the core of an electromagnet and the number of ampère turns must be so chosen that the former is sufficiently large to carry the required flux and the latter sufficient to supply the magnetomotive force necessary to magnetise the sample to the required degree. Experiments have shown that the degree of magnetisation is not critical. The magnetising force must be ample, but no increase in sensitivity is obtained if it is increased beyond quite moderate limits.

**The Effect on the Endurance Limit of Submerging Fatigue Specimens in a Cold Chamber.** O. H. Henry and T. D. Coyne. (Welding Journal, 1942, vol. 21, May, pp. 249-S-254-S). As a preliminary step to the study of the properties of welds at low temperatures, the authors carried out an investigation of the fatigue strength of specimens of a 0.25% carbon steel at temperatures of 20°, 0°, -40°, -20°, -60° and -70° C. The endurance limit was determined by Stromeier's method, in which the specimen is subjected to repeated stress cycles and the temperature is measured at regular intervals; the temperature rises steadily with the number of cycles while the metal is in the elastic state, but when the semi-plastic state is reached, the temperature rises much more rapidly; the stress indicated by the knee of the curve is taken as the endurance limit. For the low-temperature tests the specimen passed through an insulated chamber into which iced alcohol was poured, the testing stand being fixed at 45° to the horizontal with this chamber at the lower end. From the data obtained curves were constructed showing the maximum and minimum values of the endurance limit at the different temperatures. These curves indicated that with decreasing temperature the endurance limit of the steel tested increased fairly uniformly by about 0.2% per degree Centigrade. Several of the original stress-temperature curves indicated a cooling of the specimen just before the endurance limit was reached, particularly in the tests run at -60° and -70° C.; the stresses at which this cooling occurred were all higher than the endurance limit at room temperature.

**The Hardness Test as a Means of Estimating the Tensile Strength of Metals.** W. J. Taylor. (Journal of the Royal Aeronautical Society, 1942, vol. 46, Aug., pp. 198-209). The author discusses to what extent hardness test data can be used as a means of estimating the tensile strength of metals used in aircraft production. He presents several series of graphs in which the results of tensile tests are plotted against Brinell and diamond-pyramid hardness numbers



for carbon steels, low-alloy steels and non-ferrous alloys. In the case of a number of steel bars and forgings, the slope of the lines through the maximum and minimum values suggest that the tensile strength can reasonably be expected to lie between 0.20 and 0.23 times the diamond-pyramid hardness number. If the steel is known to be of a particular class the limiting values of the multiplier will be much closer.

**Hardenability of Steels Calculated.** M. A. Grossmann. (Metal Progress, 1942, vol. 42, July, pp. 80-81, 124-126). The author presents and explains a data sheet the purpose of which is to enable the hardenability of steel to be calculated from its grain size and chemical composition. The first series of curves on the data sheet enables the "ideal diameter" to be read off from the grain size and carbon content, ignoring the other elements (the ideal diameter is the size of bar which would harden through to the centre to a 50% martensitic structure if the surface were instantly quenched to 70° F.). Other curves on the data sheet give the factors for the other elements present, by which the ideal diameter is to be multiplied so as to arrive at the hardenability index for the desired composition.

**Effects of Eight Complex Deoxidizers on some 0.40 per Cent. Carbon Forging Steels.** G. F. Comstock. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1417: Metals Technology, 1942, vol. 9, Jan.). The author reports the results of mechanical and hardenability tests and grain-size determinations on laboratory heats of 0.40% carbon steel treated with the following deoxidisers: (a) Three manganese-silicon-aluminium-titanium alloys with and without boron and calcium; (b) three titanium-aluminium ferro-alloys with vanadium, molybdenum and zirconium respectively; (c) an aluminium-zirconium ferro-alloy; and (d) ferro-boron. The general conclusions were: (1) Treating a steel containing carbon 0.40% and manganese 1.15% with ferrobore increased the hardenability but coarsened the grain size giving only moderate tensile properties; (2) treatment of the steels with deoxidisers (b) gave a fine grain size, rather low hardenability and fair tensile and impact properties; (3) treatment with deoxidisers (a) containing boron resulted in a fine grain size, good hardenability and excellent tensile and impact properties; (4) treatment with deoxidiser (c) resulted in rather low hardenability and high ductility; (5) the amount of boron to be added to 0.40% carbon steels to secure good hardenability and toughness appears to be about 0.002-0.007%; and (6) it is advantageous to add the boron in the form of a complex titanium alloy rather than as ferro-boron.

**The Sliding Properties of Cast Iron Guides.** H. Opitz and K. Escher. (Giesserei, 1942, vol. 29, July 24, pp. 253-254). The authors discuss the results of tests on the wear of cast-iron guides. The following conclusions were arrived at: (1) A condition of



equilibrium is reached between the pressure on the sliding surfaces, the speed and the method of running-in; (2) during the running-in period the pressure on the surfaces in contact should be gradually increased up to the working pressure; (3) it is impossible to attain the run-in condition by running the machine idle; (4) the hardness of the two contact surfaces should always be unequal; (5) increasing the mean silicon content of the two parts in contact increases the rate of wear; (6) increasing the mean carbon content decreases the wear; and (7) increasing the mean phosphorus content decreases the wear.

**Engineering Properties of Heat-Resistant Alloys.** H. S. Avery, E. Cook and J. A. Fellows. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1480: Metals Technology, 1942, vol. 9, Aug.). The authors report on their investigation of the properties of 26/12 chromium-nickel type of steel at temperatures between 1400° and 2000° F. Between 0.20% and 0.40% of carbon the creep strength is approximately doubled by an increment of 0.10% of carbon with a simultaneous reduction in the ductility. At 1800° F. the limiting creep strength varies directly with the carbon content up to nearly 0.50% carbon. Ferrite-forming elements such as chromium, silicon, tungsten or molybdenum can be employed to increase the ductility at the expense of tensile strength; on the other hand, nickel, nitrogen and carbon increase the strength at the expense of ductility. Differences in the strengths of alloys with varying amounts of ferrite suggested that magnetic permeability measurements could be used to predict the probable creep strength of this type of alloy. Some curves in which the limiting creep strength at 1800° F. is plotted against the magnetic permeability after creep testing at this temperature are presented and indicate that this method of prediction is feasible.

**Alloy-Steel Castings, Their Properties and Application.** H. Juretzek. (Giesserei, 1942, vol. 29, June 26, pp. 217-226; July 10, pp. 243-249). The author reviews the properties of alloy-steel castings for the following applications: aircraft, motor transport, boilers, turbines and chemical plant where a high resistance to acids, wear and heat is required. He deals mainly with steels alloyed with chromium, nickel, molybdenum, manganese and silicon either separately or in combination.

**Utilisation of Bessemer Steel for Some Sections and Other Products.** S. Loshchilov and B. Fastovskiy. (Iron and Steel Institute, 1942, Translation Series, No. 100). An English translation is presented of a Russian paper which appeared in Stal, 1940, No. 2, pp. 17-22.

**Heat Treated Rails Widely Used in Great Britain.** C. J. Allen. (Metal Progress, 1942, vol. 41, May, pp. 671-675, 694). The author reviews the development in Great Britain of rails of improved quality and long life. He refers to changes of specification in 1931 by the London and North Eastern Railway Co., when the manganese limit of 0.80% max. was changed to 1.20% max. with a minimum

of 0.90%, and the carbon content was reduced to 0.50–0.60% for basic open-hearth steel and to 0.40–0.50% for acid Bessemer steel. Details of the Sandberg process of quenching the railhead immediately after rolling in order to produce a sorbitic structure are given, together with data on the changes in hardness and tensile properties caused by this treatment.

**Low-Alloy, Low-Carbon Steel in Aircraft Construction.** W. F. Sherman and T. C. Campbell. (Iron Age, 1942, vol. 150, July 2, pp. 62–67). The authors discuss the use of steel sheet and strip containing maximum 0.12% of carbon and 0.60% of manganese in the construction of aeroplanes for training purposes. The tensile properties of the steel are given, and some features of design are described and illustrated.

## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 186 A–187 A)

**The Training of the Young Metallurgist.** D. G. P. Paterson. (Sheet Metal Industries, 1942, vol. 16, June, pp. 771–781, 786; July, pp. 959–964, 968; Aug., pp. 1132–1135, 1144). Continuation of a series of articles (*see* p. 124 A). In Part III. the author discusses how metals solidify, the preparation of specimens for micro-examination, the Beilby layer, the construction of the Vickers projection microscope, face-centred and body-centred lattice structures, the deformation of crystals, the structure of copper-nickel alloys and the iron-carbon equilibrium diagram. Part IV. is devoted to the principles of spectrographic analysis, sulphur printing, the structure of killed and rimming steel ingots, deep-etching, the structure of carbon steel sheets and the casting of brass. In Part V. methods of investigating the causes of defects in brass, aluminium and steel sheet are dealt with and information on stretcher-strain markings on steel sheet is given.

**Surface Replicas for Use in the Electron Microscope.** V. J. Schaefer and D. Harker. (Journal of Applied Physics, 1942, vol. 13, July, pp. 427–433). The authors describe a technique for producing synthetic-resin replicas of the etched surfaces of metals for study in the electron microscope. The metal surface to be studied is cleaned and then coated with a very thin, slightly wedge-shaped film of polyvinyl formal, having a thickness range of about 500–750 Å in 2.5 cm. The film is removed by placing the coated surface under water and peeling the film from it. Several procedures are described for checking the thickness of such films.

**New Lead-Screen X-Ray Technique.** H. R. Isenburger. (Steel, 1942, vol. 110, June 15, pp. 81–84). The author describes some X-ray tests on aluminium and steel specimens which illustrate the advantages of using lead intensifying screens.

**Carbides in Low-Chromium Steel.** W. Crafts and C. M. Offenhauer. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1436: Metals Technology, 1942, vol. 9, Feb.). The authors report on their investigation of the formation of carbides in a series of steels containing up to 0.60% of carbon and up to 7.5% of chromium after quenching and tempering at subcritical temperatures. Specimens for X-ray examination were completely descaled, and the carbides were separated out electrolytically using 5% HCl and a platinum cathode. The following conclusions were suggested by the results obtained: (1) Chromium carbide ( $\text{Cr}_7\text{C}_3$ ) is formed at subcritical temperatures above about  $500^\circ\text{C}$ . in chromium steels containing from about 1% to more than 7.5% of chromium; within this range  $\text{Cr}_7\text{C}_3$  may be formed either directly from austenite or by the tempering of martensite and cementite; (2) when formed at below about  $500^\circ\text{C}$ . the carbide is in the form of  $\text{Fe}_3\text{C}$  at all chromium contents, and (3) in those low-chromium steels the form of the carbide is controlled by either the temperature of the austenite transformation or the tempering of the martensite.

**A New Electrolytic Isolation Method for the Determination of Iron Carbide.** E. Houdremont, P. Klinger and G. Blaschczyk. (Iron and Steel Institute, 1942, Translation Series, No. 101). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1941, vol. 15, Dec., pp. 257-270. (See p. 35 A).

**Determination of Recalescent Points in Steels.** (Metal Progress, 1942, vol. 41, June, pp. 822-824). A number of American steel producers have combined to form the Steel Standardization Group which is developing standard methods of testing the metallurgical characteristics of steel; in the present paper an account is given of the recommended method of determining the critical points and of interpreting the results. The dilatometric method is recommended as the one most easily applied in commerce and industry. The sample must be representative, cylindrical and of known analysis. The recommended heating and cooling procedure comprises: (a) Heat to  $100^\circ\text{F}$ . below the approximate  $\text{Ac}_1$ ; (b) hold at this temperature for 30 min. to obtain equilibrium conditions; (c) heat at the selected rate to  $\text{Ac}_3 + 20^\circ\text{F}$ .; (d) heat rapidly to  $150^\circ\text{F}$ . above the observed  $\text{Ac}_3$ ; (e) cool rapidly to  $20^\circ\text{F}$ . above the observed  $\text{Ac}_3$ ; and (f) cool at the selected rate to  $20^\circ\text{F}$ . below the  $\text{Ar}_1$ . When complete information is required, the determination of the critical points at the rigidly controlled rates of temperature change of  $400^\circ$ ,  $100^\circ$  and  $10^\circ\text{F}$ . per hr. is recommended. Examples are given of curves in which the logarithm of the rate of temperature change is plotted against the observed transformation temperatures; these curves are practically straight lines, and the critical points for any rate of temperature change can easily be determined from them.



**Lattice Relationships in Decomposition of Austenite to Pearlite, Bainite and Martensite.** G. V. Smith, jun., and R. F. Mehl. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1459; Metals Technology, 1942, vol. 9, Apr.). The authors describe an investigation of the atomic-crystallographic relationships existing between austenite and its decomposition products. The orientation relationships between the ferrite in bainite and austenite were determined in a plain carbon eutectoid steel by the pole-figure method. Bainite formed at  $450^{\circ}$  and  $350^{\circ}$  C. displayed the Nishiyami relationship; bainite formed at  $250^{\circ}$  C. displayed the Kurdjumow-Sachs relationship. Martensite was shown to exhibit the Kurdjumow-Sachs relationship. X-ray diffraction pictures of the cementite in pearlite, bainite and tempered martensite were obtained, but the orientations of cementite were not determined. There is evidence that cementite in bainite must be in a very fine state of subdivision. The habit planes of bainite formed at several temperatures, and of martensite were determined and the results confirmed the previous work of Greninger and Troiano. The habit plane varied markedly with the temperature of reaction although the orientation relationships remained practically constant. Metallographic studies suggested that bainite forms by a process of nucleation and growth.

**Recrystallization of Silicon Ferrite in Terms of Rate of Nucleation and Rate of Growth.** J. K. Stanley and F. Mehl. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1438; Metals Technology, 1942, vol. 9, Feb.). The authors discuss methods by which the rate of nucleation and the rate of grain growth during recrystallisation can be determined, and methods of constructing the isothermal recrystallisation curve from the rates of nucleation and growth. They applied these methods to the recrystallisation at  $770^{\circ}$  C. of silicon ferrite containing 1% of silicon after 4% deformation by elongation. The rate of nucleation was found to increase with time, probably passing through a maximum; the rate of growth remained unchanged with time. It was observed that ageing at room temperature before annealing for recrystallisation caused a marked decrease in the rate of nucleation.

**Structural Diagrams of Nickel Irons and Steels.** J. T. Eash and N. B. Pilling. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1432; Metals Technology, 1942, vol. 9, Feb.). The authors present the results of an investigation of the structure of a wide range of cast nickel steels and nickel cast irons containing up to 4% of carbon and up to 30% of nickel at three levels of silicon, namely, 0.25%, 1.5% and 3.0%. Three constitutional diagrams constructed from microscopical examinations of sections of 1.2 in.-dia. cast bars, one for each silicon level, are presented. It was evident that the amount of carbon in solid solution had a profound influence upon the matrix structure, and



this carbon in conjunction with nickel promoted the formation of austenite. Among the steels with medium nickel contents, those with greater amounts of carbon in solution became martensitic, whilst those with little carbon in solution were apt to contain bainite.

**Modifications in the State and the Properties of Iron-Nickel-Aluminium Magnet Alloys due to Heat Treatment.** W. Dannöhl. (Iron and Steel Institute, 1942, Translation Series, No. 103). This is an English translation of a paper which appeared in *Archiv für das Eisenhüttenwesen*, 1942, vol. 15, Feb., pp. 379-392. (See p. 78 A).

## CORROSION OF IRON AND STEEL

(Continued from pp. 187 A-192 A)

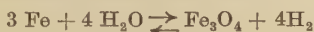
**Practical Corrosion Tester for Chemical Engineers.** M. H. Heeren. (Chemical and Metallurgical Engineering, 1942, vol. 49, Feb., pp. 126-127). The author describes and illustrates a corrosion testing machine which is capable of submitting specimens to a great variety of conditions of attack. The specimens, usually of metal strip  $3 \times \frac{1}{2}$  in., are carried on an endless chain driven by an electric motor. One cycle of the chain takes 85 min., during which the specimen passes through : (a) A short-immersion tank ; (b) a forced draft chamber ; (c) a long-immersion tank ; (d) a radiant heat chamber ; and (e) a spraying chamber. Any desired solution can be used for items (a), (c) and (e) and the temperature of the chamber (d) can also be varied.

**The Determination of Corrosion Resistance by Means of Potential Measurements, with Some Notes on Measurements on Phosphatised Steel Sheets.** F. Müller and L. Hasner. (Korrosion und Metallschutz, 1941, vol. 17, July, pp. 229-236). The authors discuss the theory underlying the study of corrosion by potential measurement and review the literature on the subject. In conclusion they briefly report on their study of the application of this method of measuring corrosion resistance to iron phosphatised by the Bonderising and the Atramentol processes and subjected to various after-treatments. They state, however, that the time-potential curves obtained, which are reproduced in the paper, do not yet allow of any definite conclusions.

**Theory of Oxidation and Tarnishing of Metals. II. Growth Laws under More General Conditions.** O. H. Hamilton and H. A. Miley. (Electrochemical Society, Apr., 1942, Preprint No. 81-31). In Part I. of this paper (see p. 128 A) it was shown that an electrochemical interpretation of the ionic theory provided a basis for developing the linear, parabolic and logarithmic laws governing the

corrosion of metals. In the present paper the laws governing the growth of films on metals under more general conditions than those dealt with in Part I. are discussed. When the electrical resistances are small, the growth rate may be controlled by some mechanical limitation. Since the linear law, for such a condition, is obeyed only when the controlling factor imposes a constant rate of growth this law will apply only seldom. It is shown that contradictions are involved in the assumptions usually made in deriving the parabolic growth law and that, from a theoretical point of view, the actual growth curve may depart widely from a parabolic curve. It cannot, however, be predicted that it would be a logarithmic curve.

**The Effect of the Physical State of the Solid Reactants on the Equilibrium of  $\text{Fe}/\text{Fe}_3\text{O}_4$  with  $\text{H}_2\text{O}/\text{H}_2$ .** R. Fricke, K. Walter and W. Lohrer. (*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, 1941, vol. 47, July, pp. 487–500). In connection with a series of investigations on active substances the authors studied the equilibrium of the reaction



at temperatures between  $360^\circ$  and  $550^\circ \text{C}$ . The iron used for the investigation, which was prepared by the reduction of ferric hydroxide at temperatures between  $450^\circ$  and  $665^\circ \text{C}$ ., was in various states of activity. Active iron led to smaller equilibrium constants ( $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ) and greater heat evolution than inactive iron. The effect of the solubility of hydrogen in the various qualities of iron used on the quantity of heat developed is discussed at some length.

**The Corrosion of Ovifak Iron under Cover.** C. Benedicks and H. Löfquist. (*Korrosion und Metallschutz*, 1941, vol. 17, Sept., pp. 320–323). The authors give an explanation for the observation that “Ovifak” iron (iron found on Disko island to the south of Greenland) is corroded after a short period when kept indoors, although it is exceptionally stable in the open air. They found that in a relatively dry atmosphere cracks developed within certain secondarily formed areas rich in hydroxide. In these cracks rust is stated to be formed owing to electrolytic corrosion of iron in contact with  $\text{FeS}$ .

**A Note on the Phenomena Involved in the Rusting of Cast Iron.** F. Roll. (*Korrosion und Metallschutz*, 1941, vol. 17, Sept., pp. 329–331). The author studied the corrosion of three qualities of high-carbon cast irons exposed for 1000 hr. at  $90$ – $98^\circ \text{C}$ . to air saturated with water vapour. He found on all specimens two distinctly separated layers of rust; the top layer consisted of bright brown ferric hydroxide, and the second layer, which in all cases was the thinner one, was black-brown and composed of a mixture of ferrous and ferric hydroxides embedded in graphite.

**Rust Protection Studied.** (Sheet Metal Industries, 1942, vol. 16, Sept., pp. 1308, 1318). A brief description is given of a special balance which is used to study the rate at which oxides form on

small samples of steel. The moving arm of the balance is a piece of quartz 6 in. long and  $\frac{1}{16}$  in. in dia. suspended by a very fine thread of tungsten wire, the whole instrument being sealed in a glass tube. Movements of the balance are observed through a microscope. A small amount of oxygen is admitted to the tube, and the changes in weight of the sample are recorded every few minutes.

**The Effect of an Electric Current on the Attack of Iron by Acids in the Presence of Inhibitors.** W. Machu and O. Ungersböck. (Korrosion und Metallschutz, 1941, vol. 17, Sept., pp. 324-329). The authors studied the attack of acids, to which organic inhibitors (in most cases dibenzyl sulphoxide) had been added, on iron made anodic or treated as secondary electrode. They determined the current-voltage curves and the losses in weight. The results obtained, which are presented in numerous tables and diagrams, indicate that, although dibenzyl sulphoxide is present as anion in acid solution, its effect is considerably greater at the cathode than at the anode. Inhibitors decrease the losses in weight also of secondary electrodes, their effect at the cathode side greatly exceeding that at the anode side. The results of the investigation are said to form a further proof of the correctness of Machu's theory on the effect of pickling inhibitors (*see* Journ. I. and S.I., 1937, No. I., p. 229 A).

**Distribution of Attack on Iron or Zinc Partly Immersed in Chloride Solutions.** U. R. Evans. (Nature, 1942, vol. 150, Aug. 1, p. 151). If iron or zinc is partly immersed in sodium or potassium chloride solution, corrosion occurs first at a zone somewhat below the water-line, but long-period tests show that finally both metals become more attacked at the water-line than anywhere else. The violent attack at the zone previously immune lends colour to the suggestion that the mechanism of corrosion in the later stages is different from that in the early stages. In this letter the author puts forward, by introducing the essential distinction between probability and conditional velocity, a common explanation for the two positions of attack.

**What Metals to Use with Acetic Acid.** F. Pavlis and F. A. Rohrman. (Chemical and Metallurgical Engineering, 1940, vol. 47, Nov., pp. 779-780). The authors report the general conclusions arrived at from the data obtained in over 2000 tests of the corrosive effect of acetic acid on different metals and alloys. Their conclusions were: (1) Hot concentrated acetic acid is an active corroding medium against most metals; (2) it has the most corrosive effect in the anhydrous state; (3) silver, tantalum, platinum and an alloy steel containing chromium 26% and molybdenum 4% are most resistant to acetic acid at all temperatures; (4) the resistance of straight chromium irons increases with increasing chromium content, whilst additions of nickel reduce the corrosion resistance; and (5) the resistance of 18/8 stainless steel decreases with increasing carbon content but is greater if molybdenum is added.

**The Corrosion of Zinc Coatings.** H. Bablik. (Korrosion und Metallschutz, 1941, vol. 17, July, pp. 250-253). The author reviews the literature on the corrosion of zinc coatings and arrives at the conclusion that the behaviour of coatings produced by hot-dipping and by electro-galvanising is practically the same.

**A Note on the Corrosion of Hardening Baths Made of 30% Chromium Cast Steel.** F. Roll. (Korrosion und Metallschutz, 1941, vol. 17, Sept., pp. 331-333). The author discusses the causes and the prevention of the corrosion of containers made of 30% chromium, 1% carbon cast steel, which have proved satisfactory in practice for salt-baths for the hardening of high-speed steel. He states that frequently four separate corroded zones can be observed on the containers, and that overheating and creeping of the molten salts are the most dangerous factors leading to corrosion.

## ANALYSIS

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(Continued from pp. 157 A-159 A)

**The Use of the Spekker Photo-Electric Absorptiometer in Metallurgical Analysis.** E. J. Vaughan. (Institute of Chemistry, Mar., 1941). The author describes in detail the development at the Admiralty laboratory, Sheffield, of the Spekker photo-electric absorptiometer and its application to make rapid determinations of small amounts of elements present in steels. The apparatus consists essentially of a light source, two photo-electric cells and a galvanometer. A 100-watt lamp emits light in two directions. To the right, the light passes through a filter and a calibrated variable aperture to a lens which yields a parallel beam of light; the beam passes through the solution of the sample contained in a glass cell, and then falls on another lens which forms an image of the lamp filament on the indicating photocell. The calibrated aperture enables the intensity of the light falling on the photocell to be varied by known amounts. To the left, light from the lamp passes through a glass cell containing water, a filter, and an iris diaphragm into a compensating photocell. The two photocells are connected in opposition across a galvanometer, so that, when the currents given by them are equal, the galvanometer shows zero deflection. A reading is taken by finding the aperture required to allow sufficient light to fall on the indicating photocell to neutralise that falling on the compensating photocell, the iris diaphragm having been set in a selected position.

**Further Advances in the Use of the Spekker Photo-Electric Absorptiometer in Metallurgical Analysis.** E. J. Vaughan. (Institute of Chemistry, Feb., 1942). Since describing the development of the Spekker photo-electric absorptiometer in an earlier paper (see preceding abstract), over 8000 determinations have been made with



it in the steel laboratory and over 7000 in the non-ferrous laboratory. In the present paper the author describes further application of absorptiometric methods under the four main headings: (1) New difference methods and the revision and extension of old methods; (2) methods of special application; (3) microanalysis; and (4) alternative sources of illumination.

**Chemical Analysis. I. Polarographic Theory and Procedure.** H. J. S. Sand. (Electrical Review, 1942, vol. 131, Sept. 4, pp. 297-300). The author briefly traces the development of the polarograph by Heyrovsky and Shikata, and discusses some simplified smooth-curve polarograms obtained from sodium-chloride solutions. Some English and American polarographs and the procedure for carrying out the analysis are briefly described.

**Analytical Control of Nickel-Plating Solutions.** E. E. Halls. (Bureau of Information on Nickel: Metallurgia, 1942, vol. 26, June, pp. 65-69). The author describes methods of making control analyses of nickel-plating solutions, basing his information on a recent brochure, "American and Continental Practice in Nickel Deposition," issued by the Bureau of Information on Nickel. The methods are divided into six groups for determining total nickel, total chloride, total sulphate, total ammonia, boric acid and acidity, alkalinity or pH value respectively.

## BOOK NOTICES

(Continued from p. 193 A)

Low, B. B. "*Engineering Mechanics*." Dealing mainly with Kinematics and Dynamics and being a companion volume to D. A. Low's "*Applied Mechanics*." A Text-Book for Engineering Students. 8vo, pp. vii + 252. Illustrated. London, 1942: Longmans, Green & Co. (Price 12s. 6d.)

This volume is complete in itself, although reference is made to its companion volume, "*Applied Mechanics*," in a few places to avoid unnecessary duplication. The book is chiefly concerned with kinematics and dynamics, including instantaneous centres, velocity and acceleration diagrams, analysis of cams, motion of rigid bodies in two dimensions, and vibrations of various kinds. In view of the importance of dimensions and dynamical similarity, a chapter is devoted to these subjects. The chapter on the deflection of beams is complete in itself but supplements to some extent the corresponding chapter in "*Applied Mechanics*"; each problem is examined from first principles and the Macaulay method is explained with examples. The contents are as follows: (1) Velocity—Acceleration—Vectors, (2) Velocity Diagrams—Instantaneous Centres, (3) Analysis of Velocity and Acceleration, (4) Acceleration Diagrams, (5) Force, Torque, Work and Energy, (6) Dimensions—Dynamical Similarity, (7) Simple Harmonic Motion, (8) Analysis of Cams, (9) Motion of Rigid Bodies in Two Dimensions, (10) Vibrations, (11) Deflection of Beams.

Low, D. A. "*A Pocket-Book for Mechanical Engineers.*" Edited by B. B. Low. New Edition Revised. Sm. 8vo, pp. xii + 778. Illustrated. London. 1942: Longmans, Green & Co. (Price 15s.)

This well-known reference book made its first appearance in 1898, and has maintained its high standard of accuracy and usefulness throughout the various editions which have appeared from time to time. The chief alterations in the present revised edition concern Weights and Measures. Many tables and values have been entirely recalculated, using the most accurately known factors. For the conversion of inches to millimetres the N.P.L. value has been adopted, as it is said to be the most accurate for scientific work. A most useful work of reference for the mechanical engineer.

ROLFE, R. T. "*Steels for the User.*" Second edition, revised and enlarged, 8vo, pp. xi + 356. Illustrated. London, 1942: Chapman and Hall, Ltd. (Price 25s.)

Although it may not be necessary for a steel user to assimilate all the information contained in this book, it is quite certain that if all of it were absorbed by all the steel users it would be of considerable benefit to the national effort. The first chapter is devoted to a consideration of mechanical quality, and is reasonably comprehensive. It is gratifying to notice that the author has clearly defined two terms that are so frequently confused, *viz.*, stress and strain. The various other terms used, such as elasticity, plasticity, ductility, &c., are also defined with equal clarity. In the section devoted to proof-stress the author states that it may take the place of yield stress in specifications for high-carbon steels. He seems to have ignored the fact that in the case of a heat-treated high-carbon steel the elastic limit and the ultimate stress are so close together that very few laboratories will risk using an extensometer on such material, because of the danger of sudden breakage.

Chapter 2 deals in a general way with the manufacture of steel and with a few of the better-known specifications. It is not particularly interesting.

On the first reading, most steel users will probably prefer to omit Chapter 3. After a few paragraphs dealing with the iron-carbon constitutional diagram and microconstituents of steel, the author proceeds to deal with the effects of composition on properties in a way that is more interesting to the steelmaker than to the user of steel.

Bright and free-cutting steels are adequately covered by Chapter 4.

As might be expected, a considerable amount of space has been devoted to heat treatment, and there are three chapters on the subject. The most interesting chapter is probably Chapter 7, where the author deals adequately with one extremely important phase of heat-treatment, *viz.*, the transformation of austenite. His description of Bain and Davenport's S-curve is masterly. Later in the chapter grain size is considered, and the only possible comment is that it is a pity that a little more space was not devoted to the work on this subject that has been done in America.

Chapter 8 deals with case-hardening, the Shorter process and the Toco process, as well as with various building up processes. The use of steels at elevated temperatures is considered in Chapter 9, and the information will probably be adequate for most steel users.

The book concludes with chapters devoted to fatigue testing, weld testing and treatment and the general principles of selection.

The volume is well indexed.

J. FERDINAND KAYSER.

SOCIETY OF CHEMICAL INDUSTRY. "*Reports on the Progress of Applied Chemistry.*" Vol. XXVI—1941. 8vo, pp. 545. London, 1942: The Society. (Price 16s.)

This volume consists of surveys by leading authorities on the progress during the past year of applied chemistry in its numerous branches. A complete list of the contributions is as follows: General, Plant, and Machinery, by F. Rumford; Fuel, by J. Hiles and R. A. Mott; Gas, Destructive Distillation, Tar, and Tar Products, by H. Hollings and W. A. Voss; Mineral Oils, by W. W. Coulston; Intermediates and Colouring Matters, by R. Fraser Thomson; Fibres, Textiles, and Cellulose. The Protein Fibres, by C. S. Whewell; Cellulose Textile Chemistry, by J. T. Marsh and F. C. Wood; Pulp and Paper, by Julius Grant; Acids, Alkalis, Salts, &c., by P. Parrish and F. C. Snelling; Glass, by W. M. Hampton and R. E. Bastick; Ceramics, Refractories, and Cements, by H. W. Webb; Iron and Steel, by R. J. Sarjant; Non-Ferrous Metals, by Ernest S. Hedges; Electrochemical and Electrometallurgical Industries, by J. W. Cuthbertson; Fats, Fatty Oils, and Detergents, by T. P. Hilditch; Plastics, by Members of the Plastics Group; Resins, Drying Oils, Varnishes, and Paints, by Members of the Oil and Colour Chemists' Association; Rubber, by T. R. Dawson; Leather, by Michael P. Balfe; Soils and Fertilisers, by A. G. Pollard; Sugars and Starches, by E. B. Hughes; The Fermentation Industries, by Alan A. D. Comrie; Foods, by N. C. Wright and E. C. Owen; Fine Chemicals and Medicinal Substances, by Norman Evers; Essential Oils, Isolates, Derivatives and Synthetics, by W. H. Simmons; Photographic Materials and Processes, by E. G. V. Barratt, D. J. T. Howe and J. W. Glassett; Sanitation and Water Purification, by G. D. Elsdon and M. Gibson.

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# SUBJECT INDEX.

[References to the papers read before the Institute are indicated by the word *Paper* following the page number. The letter *P.* denotes a reference in Section I. of the Journal which contains the reports of the proceedings of meetings, the papers read, and the discussions thereon. The letter *A.* denotes a reference to the section dealing with abstracts.

*Indexing of Alloy Steels and Other Alloys.* In the indexing of alloy steels, carbon and iron are ignored and the alloying elements contained in the steel are arranged in alphabetical order; for example, all references to nickel-chromium-molybdenum steel will be found under the heading chromium-molybdenum-nickel steel. In the indexing of other alloys, carbon and iron, when present, are included in the title; iron, when present, is always mentioned first and the other elements follow in alphabetical order, carbon being in all cases mentioned last. Examples: "Iron-silicon-carbon alloys" and "iron-chromium-nickel-carbon alloys."]

ABRASION. *See* Wear.

ABRASIVE DISCS, use for cutting metals, 112A.

ABSORPTIOMETER, Spekker Photo-Electric, use in analysis, 227A.

ACETIC ACID, corrosion of metals, 226A.

ACID BESSEMER STEEL, dephosphorisation, 50A.

ACID OPEN-HEARTH FURNACES, refractory materials for, 162A.

ACID OPEN-HEARTH PRACTICE, 104A., 204A.

carbon control, 206A.

slag control, 206A.

use of light scrap, 206A.

ACID OPEN-HEARTH STEEL, gases in, 206A.

ACID-RESISTANT IRON, manufacture, 133A.

ACIDS :

corrosion of alloys, 125A.

corrosion of iron, effect of electric current, 226A.

corrosion of steel, 191A.

ACOUSTIC TESTS, 67A.

AGDE-DAMM TEST, for coking coal, 44A.

AIR, compressed, use in hydraulic plants at Bessemer works, 57A.

AIR CONDITIONING. *See* Blast, drying.

AIR HEATERS, use at blast-furnaces, 133A.

AIRCRAFT CONSTRUCTION :

use of castings, 49A.

use of drop forgings, 58A.

use of low-alloy steel, 74A., 221A.

use of stainless steel, 74A.

use of steel, 74A.

AIRCRAFT PARTS, heat-treatment furnaces, 173A.

AIRCRAFT STEEL, specifications, American, 34A.

ALGOMA STEEL CORPORATION, LTD. : boiler plant, 3A.

lining of basic furnaces, 42A. plant, 11A.

ALLOYS :

aluminium, damping capacity, 70A.

copper, corrosion in soils, 126A.

copper-zinc, damping capacity, 70A.

corrosion, mechanism, 125A.

determination of titanium, mercury cathode method, 82A.

iron, solubility of hydrogen, 181 *Paper*.

iron-aluminium-cobalt-nickel, use for magnets, 148A.

iron-aluminium-nickel, effect of heat treatment, 78A., 224A.

iron-aluminium-nickel, sintered, use for magnets, 46A.

iron-carbon, absorption of nitrogen, 30A.

iron-chromium, absorption of nitrogen, 30A.

iron-cobalt, corrosion, 125A.

iron-columbium, precipitation hardening and creep strength, 72A.

iron-manganese, corrosion, 125A.

iron-nickel, corrosion, 125A.

iron-nickel, damping capacity, 70A.

iron-nickel, solubility of hydrogen, 181P.

iron-phosphorus, absorption of nitrogen, 30A.



**ALLOYS (contd.)—**

- iron-silicon, acid-resistant, manufacture, 133A.
- magnesium, damping capacity, 70A.
- non-ferrous, corrosion, 125A.
- ALNICO, use for magnets, 148A.
- ALUMETISING, 182A.
- ALUMINA :
  - effect on carbon monoxide, decomposition, 3A.
  - effect on iron oxide at high temperatures, 199A.
- ALUMINIUM :
  - addition to killed steel, 206A.
  - anodic coatings, 114A.
  - consumption in American steel industry, 53A.
  - effect in free-cutting steel, machinability, 148A.
  - effect in galvanising bath on coatings, 181A.
  - oxide coatings, 114A.
- ALUMINIUM ALLOYS, damping capacity, 70A.
- ALUMINIUM COATINGS, effect on cast iron, growth and scaling, 182A.
- AMMONIUM CHLORIDE, corrosion of alloys, 125A.
- ANALYSIS, 80A., 157A., 227A.
  - electrographic, 157A.
  - gases in liquid steel, 80A.
  - iron ore, Moore's electrolytic method, 157A.
  - pig iron, 82A.
  - spectrum, determination of copper and tin, 205A.
  - spectrum, inclusions, 81A.
  - spectrum, instruments used in, 152A.
  - spectrum, iron and steel, 81A.
  - use of drop reactions, 157A.
- ANCHORS, moulding, 202A.
- ANNEALING :
  - bright, steel, 64A.
  - effect on transformer steel, 120A.
- ANNEALING FURNACES, for stainless-steel strip, 18A.
- ANODIC COATINGS, on aluminium, 114A.
- ANTIMONY, effect in galvanising bath on coatings, 181A.
- ARC FURNACES. *See* Electric Furnaces.
- ARKANSAS, manganese ore deposits, 87A.
- ARMAMENTS, steel specifications, 185A.
- ASH, determination in coal, 158A.
- ASSOCIATES, election, 4P.

- ATLANTIC STEEL Co., plant, 169A.
- ATMOSPHERES :
  - controlled, 61A., 107A., 173A., 211A.
  - industrial, determination of extent of pollution, 164A.
- ATRAMENT PROCESS, 179A.
- AUSTENITE :
  - decomposition products, lattice relationships, 223A.
  - solubility of graphite, 186A.
  - transformation in cast iron, effect of elements, 186A.
  - transformation in high-speed steel, 76A.
- AUSTENITIC STEEL, machinability, effect of elements, 148A.
- AUSTRALIA :
  - open-hearth practice, 206A.
  - production of ferro-alloys, 95A.
  - production of tungsten steel, 95A.
- AUTO SPECIALITIES MANUFACTURING Co., plant, 100A.
- AUTOMOBILE CONSTRUCTION, use of cast iron, 117A.
- AUTUMN MEETING, proceedings, 1P.
- AXLES, fatigue cracks, detection, 183A.
- BAINITE, lattice relationship to austenite, 223A.
- BAKELITE, damping capacity, 70A.
- BARRETT EFFECT, 70A.
- BARS, drawing, use of carbide dies, 13A.
- BASIC BESSEMER PLANTS, use of compressed air in hydraulic plants, 57A.
- BASIC BESSEMER PROCESS :
  - control by measurement of flame radiation, 103A., 204A.
  - heat requirements, 52A.
- BASIC OPEN-HEARTH FURNACES :
  - tilting, brick consumption, 16P.
  - tilting, linings, 9 *Paper*.
- BASIC OPEN-HEARTH PRACTICE, 103A., 204A.
  - use of blown metal, 206A.
- BASIC OPEN-HEARTH PROCESS :
  - heat requirements, 52A.
  - iron ores for, 204A.
  - slag control, 204A.
- BEACON BENTONITE SUBSTITUTE, use in moulding sand, 436P.
- BEARINGS, synthetic resin, 210A.
- BENBOND, use in moulding sand, 430P.
- BEND-FATIGUE TESTS, welded plates, 20A.

- BEND TESTS :**  
 notched-bar, 25A.  
 weld metal, 20A., 67A.
- BENTONITE**, use in moulding sand, 423P.
- BERYLLIUM OXIDE**, effect on iron oxides at high temperatures, 199A.
- BESSEMER CONVERTERS**, pin distribution in bottoms, 50A., 203A.
- BESSEMER PLANTS :**  
 basic, use of compressed air in hydraulic plants, 57A.  
 lay-out, 169A.
- BESSEMER PROCESS :**  
 basic, control by measurement of flame radiation, 103A., 204A.  
 basic, heat requirements, 52A.  
 effect of after-blow, 203A.
- BESSEMER STEEL :**  
 acid, dephosphorisation, 50A.  
 effect of phosphorus, 122A.
- BIBLIOGRAPHY**, 84A., 159A., 230A.  
 microbiological deposits in water circulating systems, 189A.
- BILLET MILLS**, electric driving, 14A.
- BILLETS :**  
 descaling, 22A., 176A.  
 reheating furnaces, 209A.  
 rolling, costs, 141A.
- BISMUTH**, effect in steel, machinability, 148A.
- BLAST :**  
 control in cupolas, 200A.  
 design of valves and mains, 198A.  
 drying, 7A., 166A.  
 effect of moisture and pre-heating on cast iron, 97A.  
 use of air-heaters, 133A.
- BLAST-FURNACE COKE**, properties, 44A.
- BLAST-FURNACE FLUE DUST :**  
 concentration, 166A.  
 recovery of iodine and potassium chloride, 199A.  
 sintering, 195A.
- BLAST-FURNACE GAS :**  
 calculation of carbon-monoxide, carbon dioxide and hydrogen contents, 45A.  
 cleaning, 6A.  
 use in conjunction with coke breeze for firing boilers, 163A.  
 use under boilers, 197A.
- BLAST-FURNACE LININGS**, wear, 162A.
- BLAST-FURNACE PLANT :**  
 Algoma Steel Corporation, Ltd., 11A.  
 Steel Company of Canada, Ltd., 137A.
- BLAST-FURNACE PRACTICE :**  
 Broken-Hill Proprietary Co., Ltd., 93A.  
 effect of coke properties, 7A.  
 United States, 2A.
- BLAST-FURNACE SLAG :**  
 air-cooled, specification, 167A.  
 "falling," 21 *Paper*.  
 foamed, properties and uses, 7A.  
 recovery of vanadium, "bottom-reaction" process, 45A.  
 uses, 94A.
- BLAST-FURNACE SLAG CEMENT**, 46A., 199A.
- BLAST-FURNACES :**  
 blast, drying, 7A., 166A.  
 blast, use of air-heaters, 133A.  
 blowing-out, 45A.  
 charging, 198A.  
 hearths, carbon blocks for, 162A.  
 refractory materials, 90A.  
 use of sinter, 94A., 195A.
- BLISTERS**, in enamel coatings on steel, 115A.
- BLOOMS :**  
 descaling, 23A.  
 reheating furnaces, 209A.
- B.M. ROLLING MILLS, LTD.**, plant, 142A.
- BOILER PIPES**, specification, British, 152A.
- BOILER PLANT**, Algoma Steel Corporation, Ltd., 3A.
- BOILER PLATE**, recrystallisation during hot-working, 68A.
- BOILER STEEL :**  
 intercrystalline cracking, 155A.  
 specification, British, 34A.
- BOILER TUBES**, pressure and creep tests, 28A.
- BOILER WATER**, microbiological deposits, 189A.
- BOILERS :**  
 use of blast-furnace gas, 197A.  
 use of blast-furnace gas and coke breeze, 163A.  
 waste-heat, 4A.
- BOLTS :**  
 corrosion in soils, 126A.  
 heat treatment, 18A.
- BOMBS :**  
 heat-treatment furnaces, 18A.  
 moulding, 136A.
- BOOK NOTICES :**  
 Institute of Engineers, Australia, "Australian Standard Engineering Drawing Practice," 84A.  
 Low, "Engineering Mechanics," 228A.

BOOK NOTICES (*contd.*)—

- Low, "Pocket Book for Mechanical Engineers," 229A.
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- Meyenberg, "Economic Control of Iron and Steel Works," 39A.
- Pigott, "Chemical Analysis of Ferrous Alloys," 128A.
- Rolfe, "Steels for the User," 2nd ed., 229A.
- Sisco, "Modern Metallurgy for Engineers," 130A.
- Society of Chemical Industry, "Reports on Progress of Applied Chemistry," Vol. XXVI, 230A.
- BORON, effect in steel and cast iron, 121A.
- BOTTOM-REACTION PROCESS, for recovery of vanadium, 45A.
- BRAKE DRUMS, cast iron, behaviour, 134A.
- BRASS, corrosion in soils, 127A.
- BRAZIL :  
iron and steel plant, 11A.  
production of ferro-alloys, 199A.
- BRIDGES :  
for handling ore, 2A.  
welded, cracks in, 21A.
- BRIQUETTING, iron ore, 206A.
- BRITISH CAST IRON RESEARCH ASSOC., permeability test for moulding sand, 416P.
- BRITISH IRON AND STEEL FEDERATION, work on fuel economy, 91A.
- BRITISH STANDARD SWELLING TEST, for coal, 164A.
- BRITISH STANDARD TEST CODE, for coke ovens, 92A.
- BRITTLENESS :  
chromium-molybdenum-nickel steel at high temperatures, 29A.  
chromium-molybdenum steel at high temperatures, 29A.  
chromium steel at high temperatures, 29A., 71A.  
steel, effect of hydrogen, 30A.  
structural steel, effect of elements, 32A.
- BROEMEL STRIP MILL, 14A., 141A.
- BROKEN HILL PROPRIETARY CO., LTD. :  
blast-furnace practice, 93A.  
coking practice, 93A.
- BRONZE, damping capacity, 70A.
- BRONZE-WELDING, cast iron, 175A.
- BROWN SYSTEM, of fuel-rate control for furnaces, 206A.
- "BRUCH," definition, 119A.
- BUFFALO BOLT CO., pickling plant, 112A.
- BULLET-PROOF STEEL, production, 171A.
- BULLETS, armour-piercing, case-hardening, 107A.
- BUREAU OF MINES—AMERICAN GAS ASSOCIATION TESTS, of coking coal, 918A.
- BUSHES, manufacture from iron powder, 46A.
- BY-PRODUCTS, recovery, 5A.
- CADMIUM :  
effect in galvanising bath on coatings, 181A.  
electrodeposition, 113A.
- CADMIUM COATINGS, on wrought iron, corrosion in soils, 126A.
- CALCIUM, effect in high-sulphur iron, 37A.
- CALCIUM - ALUMINIUM - MAGNESIUM SILICATES, quaternary system, 36P.
- CALCIUM-ALUMINIUM SILICATES, ternary system, 43P.
- CALCIUM SILICATES, desulphurising power, effect of manganese, 138A.
- CALIFORNIA, tungsten ore deposits, 1A.
- CALIFORNIAN CHROME ORE, plasticity, 205A.
- CANNON, cast iron, first produced in England, 131 *Paper*.
- CAPILLARITY, in grain boundaries, effect on grain growth, 36A.
- CARBIDE TOOLS, 22A.
- CARBIDES, formation in chromium steel, 222A.
- CARBON :  
control, in acid open-hearth practice, 206A.  
deposition in coke-oven roofs, 197A.  
determination in iron and steel, 157A.  
determination, use of Leco apparatus, 205A.  
diffusion in rimming steel, 357 *Paper*.  
effect in cast iron, 31A.  
effect in cast iron, austenite transformation, 187A.  
effect in cast iron, machinability, 148A.  
effect in molybdenum steel, creep strength, 149A., 150A.

**CARBON (contd.)—**

- effect in steel, hair-line crack formation, 229P.
- effect in steel, machinability, 27A.
- effect in structural steel, brittleness, 32A.
- effect in vanadium steel, creep strength, 149A., 150A.
- thermal conductivity, 90A.
- CARBON BLOCKS.** *See* Refractory materials.
- CARBON DIOXIDE**, calculation of amount in blast-furnace gas, 45A.
- CARBON MONOXIDE :**
  - calculation of amount in blast-furnace gas, 45A.
  - decomposition, catalytic effect of metals and oxides, 3A.
- CARBON-OXYGEN EQUILIBRIUM** in liquid iron, 205A.
- CARBON STEEL :**
  - creep strength, effect of temperature, 27A.
  - effect of tin, 141P.
  - electrolytic cleaning, 112A.
  - hardenability, 16A.
  - properties, 216A.
  - weldability tests, 20A.
- CARBURISING**, gaseous, 30A.
- CARNEGIE-ILLINOIS STEEL CORP.**, strip mill, 15A.
- CARNEGIE RESEARCH GRANT :**
  - award to B. H. Mason, 2P.
  - award to H. J. Merchant, 2P.
- CARNOTITE ORE**, concentration, 194A.
- CARTRIDGE CASES**, steel, production, 58A.
- CASE-HARDENED STEEL**, wear tests, 147A.
- CASE-HARDENING :**
  - armour-piercing bullets, 107A.
  - chromium - manganese - molybdenum steel, 214A.
  - chromium-manganese steel, 19A.
  - chromium - manganese - vanadium steel, 214A.
  - gears, 62A.
  - low-carbon steel, 143A.
  - Nicarb process, 63A.
  - salt bath. *See* Heat Treatment.
- CASE-HARDENING STEEL :**
  - molybdenum-free, properties, 26A.
  - selection for gear manufacture, 16A.
- CAST IRON :**
  - addition of silicon briquettes, 201A.
  - alloy, elastic properties, 31A.
  - alloy additions, economical use, 134A.

**CAST IRON (contd.)—**

- austenite transformation, effect of elements, 186A.
- bronze-welding, 175A.
- carbon saturation, 215A.
- carbon saturation, effect of silicon, 122A.
- chromium-nickel, thermal cracking, 135A.
- corrosion, 225A.
- corrosion in soil, 110P.
- damping capacity, 70A.
- decarburisation, R.K. process, 7A.
- defects, 75A.
- desulphurisation, soda ash method, 98A.
- detection of alloying elements, 75A.
- effect of boron, 121A.
- effect of elements, 31A.
- effect of hydrogen, 72A.
- effect of manganese, 151A.
- effect of moisture and preheating of blast, 97A.
- effect of sulphur, 151A.
- effect of thorium, 121A.
- Emmel, properties, 31A.
- enamel coatings, defects, 115A.
- graphitisation, effect of silicon and nickel, 101A.
- growth, effect of aluminium coatings, 182A.
- high-duty, production, 48A.
- high-duty, production in cupolas, 96A.
- high-duty, thermal cracking, 135A.
- inoculated, properties, 31A.
- machinability, effect of elements, 148A.
- malleable. *See* Malleable Cast Iron.
- Maurer's diagram, 67A.
- Meehanite, properties, 31A.
- metallographic polishing, 124A.
- molybdenum, thermal cracking, 135A.
- molybdenum-nickel, production, 48A.
- nickel, structure, 223A.
- Ni-Tensile, properties, 31A.
- nitrided, use for tools, 173A.
- scaling, effect of aluminium coatings, 182A.
- undercooling, 102A.
- use for automobile construction, 117A.
- use for cylinder liners, 122A.
- wear, 219A.
- CAST IRON BOUNDARY POST**, 95A.
- CAST IRON CANNON**, first produced in England, 131 Paper.



## CASTING :

- centrifugal, 10A.
- centrifugal, guns, 49A.

## CASTINGS :

- chilled, graphitisation, 102A.
  - chromium steel, properties, 220A.
  - cleaning, 10A., 136A., 202A.
  - defects, 101A.
  - effect of molten metal conditions, 201A.
  - gating, 49A.
  - iron, large, moulding, 202A.
  - iron, substitution for steel castings, 167A.
  - malleable iron. *See* Malleable Iron Castings.
  - manganese steel, properties, 220A.
  - molybdenum steel, properties, 220A.
  - nickel steel, lowering of nickel content, 33A.
  - nickel steel, properties, 220A.
  - porosity, 49A.
  - silicon steel, properties, 220A.
  - steel, factors affecting surface, 207A.
  - steel, moulding sands for, 393 *Paper*.
  - steel, production, 98A., 135A.
  - steel, production in converters, 9A., 99A., 135A.
  - steel, production in rotary furnaces, 53 *Paper*.
  - steel, solidification, 203A.
  - steel, substitution of iron castings, 167A.
  - use in aircraft construction, 49A.
- CATENARY HEAT-TREATMENT FURNACE, 18A.
- CATHODIC PROTECTION, metals, 124A.
- CAVITATION EROSION, resistance of metals to, 37A.
- CEMENT, blast-furnace slag, 46A., 199A.
- CEMENTATION, nitro-, 63A.
- CEMENTITE, solubility curve, 186A.
- CHAFING FATIGUE, 184A.
- CHAIN-MAKING INDUSTRY, Staffordshire, 106A.
- CHILLED CASTINGS, graphitisation, 102A.
- CHILLED ROLLS, production, 201A.
- CHILLED WHEELS, production, 167A.
- CHLORIDE SOLUTIONS :
- corrosion of iron, 226A.
  - corrosion of zinc, 226A.
- CHROM-X, use in production of chromium steel, 56A.
- CHROME-MAGNESITE BRICKS. *See* Refractory Materials.

## CHROME ORE :

- plasticity, 205A.
  - position in United States, 87A.
  - uses, 42A.
  - See also* Refractory Materials.
- CHROME ORE DEPOSITS :
- Montana, 1A.
  - Oregon, 1A.
  - South America, 87A.
- CHROMGUSS, properties, 123A.
- CHROMIC OXIDE :
- effect on carbon monoxide, decomposition, 3A.
  - effect on iron oxide at high temperatures, 199A.
- CHROMITE. *See* Refractory Materials.
- CHROMIUM, determination in iron and steel, 82A., 83A.
- determination, use of photo-electric colorimeter, 205A.
  - effect in cast iron, 31A.
  - effect in cast iron, machinability, 148A.
  - effect in free-cutting steel, machinability, 148A.
  - electrodeposition, 24A., 113A.
  - electrodeposition, temperature control, 177A.
  - sponge, production, 131A.
- CHROMIUM CARBIDE, effect in cast iron, austenite transformation, 187A.
- CHROMIUM COATINGS :
- on cylinder liners and crankshafts, 147A.
  - hard, 24A.
  - properties, 177A.
- CHROMIUM - COBALT - MOLYBDENUM-NICKEL STEEL, heat treatment and welding, 151A.
- CHROMIUM-COBALT-TUNGSTEN HIGH-SPEED STEEL, properties, 22A.
- CHROMIUM - COLUMBIUM - NICKEL - TITANIUM STEEL, heat treatment and welding, 151A.
- CHROMIUM-COPPER STEEL :
- corrosion in soil, 110P.
  - weldability tests, 110A.
- CHROMIUM - MANGANESE - MOLYBDENUM STEEL, case-hardening, 214A.
- CHROMIUM - MANGANESE - NICKEL STEEL, use for wrapping wire, 33A.
- CHROMIUM-MANGANESE STEEL :
- case-hardening, 19A.
  - heat treatment and welding, 151A.
  - scaling, effect of vanadium, 18A.
- CHROMIUM - MANGANESE - VANADIUM STEEL, case-hardening, 214A.

## CHROMIUM - MOLYBDENUM - NICKEL STEEL :

- effect of tin, 141P.
- embrittlement at high temperatures, 29A.
- hair-line cracks, effect of carbon, 229P.
- hardenability, 16A.
- hardenability tests, 148A.
- heat treatment, 65A.
- heat treatment and welding, 151A.

## CHROMIUM-MOLYBDENUM STEEL :

- creep strength, effect of temperature, 27A.
- effect of tin, 141P.
- embrittlement at high temperatures, 29A.
- nitriding, 63A.
- use for rock drills, 73A.
- weldability tests, 20A.

## CHROMIUM - MOLYBDENUM - VANADIUM STEEL, properties at high temperatures, 30A.

## CHROMIUM-NICKEL CAST IRON, thermal cracking, 135A.

## CHROMIUM-NICKEL STEEL :

- cast, properties, 123A.
- corrosion, 126A.
- corrosion in hydrochloric acid, 127A.
- corrosion in nitric acid, 192A.
- effect of nitrogen, 121A.
- effect of tin, 141P.
- heat treatment and welding, 151A.
- production by duplex process, 54A.
- properties at high temperatures, 220A.

quenching after tempering, 183A.

scaling, effect of vanadium, 18A.

substitutes for, 33A.

use in nitric acid plants, 151A.

welding, 144A., 145A.

welding, Shotweld process, 110A.

## CHROMIUM-NICKEL STEEL SHEETS, properties, 146A.

## CHROMIUM-SILICON STEEL, scaling, effect of vanadium, 18A.

## CHROMIUM - SILICON - ZIRCONIUM STEEL, welding, 144A.

## CHROMIUM STEEL :

- carbide formation, 222A.
- cast, properties, 123A.
- corrosion in soil, 110P., 126A.
- effect of nitrogen, 121A.
- embrittlement at high temperatures, 29A., 71A.
- pickling, 112A.
- production, use of Chrom-X, 56A.
- scaling, effect of vanadium, 18A.

CHROMIUM STEEL (*contd.*)—

- use for magnets, 148A.
- use in nitric acid plants, 151A.
- welding, 111A., 144A.

## CHROMIUM-STEEL CASTINGS, properties, 220A.

## CHROMIUM - TUNGSTEN - VANADIUM HIGH-SPEED STEEL, properties, 22A.

## CHROMIUM-VANADIUM HIGH-SPEED STEEL, effect of molybdenum and titanium, 31A.

## CLAD STEEL :

- copper, production, 113A.
- copper-nickel, production, 113A.
- stainless, production, 113A.
- stainless, production, Jessop method, 113A.

## CLAY, use in moulding sand, 428P.

## CLAY SLURRY, addition to moulding sand, 136A.

## CLAY SUBSTANCE, nature in moulding sand, 100A.

## CLEANING :

- blast-furnace gas, 6A.
- castings, 10A., 136A., 202A.
- coal, 5A.
- electrolytic, 112A.
- gases, electrostatic precipitation, 5A.
- metals, 22A., 112A., 175A.
- steel prior to painting, 23A.

## COAL :

- agglutinating-value test, 93A.
- American, coking tests, 198A.
- caking, 164A.
- cleaning, 5A.
- coking tests, Agde-Damm method, 44A.
- coking tests, Davis Method, 44A.
- coking tests, Gieseler method, 44A., 165A.
- determination of ash, 158A.
- determination of sulphur, 83A.
- drying, Fleissner process, 197A.
- Durham, coking properties, 4A.
- Illinois, determination of fusain, 158A.
- pulverised, use in reheating furnaces, 132A.
- swelling, 164A., 165A.
- swelling tests, British Standard method, 164A.
- swelling tests, Gray-King method, 164A.
- swelling tests, Lessing method, 164A.

## COAL DEPOSITS :

- Japan, 1A., 87A.
- Korea, 1A.

**COAL DEPOSITS (contd.)—**

Manchukuo, 1A.  
 Pennsylvania, 1A.  
 South America, 87A.

**COATING, metals, 24A., 113A., 176A.****COATINGS :**

aluminium, effect on cast iron,  
   growth and scaling, 182A.  
 anodic, on aluminium, 114A.  
 cadmium, on wrought iron, cor-  
   rosion in soils, 126A.  
 chromium, hard, 24A.  
 chromium, properties, 177A.  
 copper, on iron and steel, 181A.  
 on cylinder liners and crankshafts,  
   147A.  
 enamel, on cast iron, defects,  
   115A.  
 enamel, defects, effect of hydrogen,  
   116A.  
 enamel on steel, blisters, 115A.  
 enamel, on steel, effect of oxide  
   coatings, 116A.  
 nickel, thickness determination,  
   177A.  
 oxide, on aluminium, 114A.  
 oxide, iron and steel, 114A.  
 oxide, on magnesium, 114A.  
 oxide, protective value, 192A.  
 oxide, on steel, salt-spray test,  
   154A.  
 oxide, on zinc, 114A.  
 paint, on steel, 182A.  
 paint, substitute for zinc coatings,  
   117A.  
 phosphate, 177A., 178A., 179A.  
 phosphate, on condenser tubes,  
   179A.  
 phosphate, on piston rings, 180A.  
 phosphate, protective value, 192A.,  
   224A.  
 phosphate, sprayed, 180A.  
 phosphate, on steel, 114A.  
 phosphate, on steel prior to cold-  
   work, 180A.  
 protective, for underground pro-  
   tection, 39A., 126A.  
 protective, use of greases and oils,  
   188A.  
 zinc, corrosion, 226A.  
 zinc, electrolytic, corrosion, 190A.  
 zinc, electrolytic, protective value,  
   192A.

**COBALT :**

damping capacity, 70A.  
 substitutes for, 185A.

**COBALT HIGH-SPEED STEEL, pro-  
 perties, 22A.****COHESIVE STRENGTH, metals, 119A.,  
 216A.****COKE :**

blast-furnace, properties, 44A.  
 density and porosity, determina-  
   tion, 93A.

determination of sulphur, 83A.

low-temperature, use in producers,  
 196A.

properties, effect on blast-furnace  
 operation, 7A.

**COKE BREEZE, use in conjunction with  
 blast-furnace gas for firing  
 boilers, 163A.****COKE-OVEN GAS, use in open-hearth  
 furnaces, 207A.****COKE-OVEN ROOFS, carbon deposi-  
 tion, 197A.****COKE-OVEN WALLS, temperature  
 distribution, 92A.****COKE OVENS :**

British standard test code, 92A.  
 Koppers-Becker, heating, 92A.  
 repair, 5A.

**COKING PRACTICE, 44A.**

Broken-Hill Proprietary Co., Ltd.,  
 93A.

effect of coking rate, 197A.

**COKING PROPERTIES, Durham coal,  
 4A.****COKING TESTS :**

American coal, 198A.  
 coal, Agde-Damm method, 44A.  
 coal, Davis method, 44A.  
 coal, Gieseler method, 44A., 165A.

**COLBOND, use in moulding sand,  
 429P.****COLD ROLLING :**

cooling of rolls, 141A.  
 effect on transformer steel, 120A.

**COLD WORK :**

effect on lattice expansion, 25A.  
 effect on steel, 26A.

**COLD-WORKED MANGANESE STEEL,  
 use for magnets, 27A., 149A.****COLD-WORKING, steel, pretreatment  
 by phosphatising, 180A.****COLORADO, tungsten ore deposits, 1A.****COLORIMETER, photo-electric, use in  
 analysis, 205A.****COLOURING, metals, 113A., 182A.****COLUMBIUM :**

effect in steel, machinability, 148A.  
 effect in structural steel, brittle-  
   ness, 32A.  
 in South America, 87A.

**COLUMBIUM STEEL, creep strength,  
 72A.****COMPANHIA SIDERURGICA BELGO-  
 MINEIRA, plant, 11A.****COMPRESSIVE PROPERTIES, stainless  
 steel sheets, 146A.**

## CONCENTRATION :

carnotite ore, 194*A*.  
 flue dust, 166*A*.  
 iron ore, 2*A*.  
 lead ore, 89*A*.  
 manganese ore, 41*A*., 88*A*., 89*A*.,  
 131*A*., 194*A*.  
 manganiferous iron ore, 88*A*.  
 mercury ore, 89*A*.  
 strontium ore, 89*A*.  
 titanium ore, 89*A*.  
 vanadium ore, 89*A*.  
 wad ore, 195*A*.  
 zinc, 89*A*.

CONDENSER TUBES, phosphate coat-  
 ing, 179*A*.

CONDENSING PLANT, corrosion, 189*A*.

## CONDUCTIVITY :

thermal, carbon, 90*A*.  
 thermal, fibrous material, 90*A*.  
 thermal, granular material, 90*A*.  
 thermal, graphite, 91*A*.  
 thermal, insulating bricks, 90*A*.  
 thermal, mica, 90*A*.  
 thermal, moulding sand, 420*P*.  
 thermal, refractory materials, 90*A*.

CONTRACTION, malleable cast iron,  
 48*A*.

## CONTROL INSTRUMENTS :

for rolling-mill plants, 16*A*.  
 for steel plants, 137*A*.

## CONVERTERS :

compared with electric furnaces,  
 54*A*.  
 pin distribution in bottoms, 50*A*.,  
 203*A*.  
 production of steel castings, 9*A*.,  
 99*A*., 135*A*.

## COPPER :

corrosion in soils, 126*A*., 127*A*.  
 determination in iron and steel,  
 158*A*.  
 determination, spectrographic  
 method, 205*A*.  
 effect in cast iron, 31*A*.  
 effect in cast iron, machinability,  
 148*A*.  
 elastic properties, 119*A*.  
 electrodeposition, 113*A*.  
 spraying, 181*A*.

COPPER ALLOYS, corrosion in soils,  
 126*A*.

COPPER CLAD STEEL, production,  
 113*A*.

COPPER COATINGS, on iron and steel,  
 181*A*.

COPPER-MOLYBDENUM STEEL, corro-  
 sion in soils, 126*A*.

COPPER-NICKEL CLAD STEEL, pro-  
 duction, 113*A*.

## COPPER STEEL :

corrosion in soil, 110*P*.  
 forgeability, 150*A*.  
 weldability, 150*A*.

COPPER-ZINC ALLOYS, damping capa-  
 city, 70*A*.

COPPERWELD STEEL Co., plant, 203*A*.

## CORE BINDERS :

economical use, 202*A*.  
 properties, 10*A*.

CORE BLOWERS, 101*A*.

CORE COMPOUNDS, 441*P*.

CORE-SAND MIXTURES, 441*P*.  
 preparation, 10*A*.

CORE SANDS, gas evolution, 446*P*.

## CORROSION :

alloys, mechanism, 125*A*.  
 atmospheric, iron, 187*A*.  
 atmospheric, steel, 191*A*.  
 bolts in soils, 126*A*.  
 brass in soils, 127*A*.  
 cast iron, 225*A*.  
 cast iron in soils, 110*P*.  
 chromium-copper steel in soils,  
 110*P*.  
 chromium-nickel steel, 126*A*.  
 chromium-nickel steel in nitric  
 acid, 192*A*.  
 chromium steel in soils, 110*P*.,  
 126*A*.  
 copper and copper alloys in soils,  
 126*A*.  
 copper in soils, 127*A*.  
 copper-molybdenum steel in soils,  
 126*A*.  
 copper steel in soils, 110*P*.  
 galvanised steel in soils, 126*A*.  
 galvanised vessels, by pig food,  
 192*A*.  
 ingot iron in soils, 110*P*.  
 iron in acids, effect of electric  
 current, 226*A*.  
 iron in chloride solutions, 226*A*.  
 iron-cobalt alloys, 125*A*.  
 iron-manganese alloys, 125*A*.  
 iron-nickel alloys, 125*A*.  
 iron and steel in soils, 107 *Paper*,  
 38*A*., 126*A*., 127*A*.  
 lead in soils, 127*A*.  
 malleable cast iron in soils, 126*A*.  
 metals in acetic acid, 226*A*.  
 non-ferrous alloys, 125*A*.  
 Ovifak iron, 225*A*.  
 pipes in soils, 39*A*.  
 prevention, use of greases and oils,  
 188*A*.  
 salt-bath containers, 226*A*.  
 sheets in soils, 39*A*.  
 stainless steel in hydrochloric acid,  
 127*A*.



CORROSION (*contd.*)—

- stainless steel in soils, 127*A*.
- steel in acids, 191*A*.
- steel in hydrochloric acid, 191*A*.
- steel in nitric acid, 191*A*.
- steel in sea water, 191*A*.
- steel in sulphuric acid, 191*A*.
- steel in water, use of inhibitors and their effect on heat transfer, 73 *Paper*.
- turbine blades, 38*A*.
- water-circulating systems, microbiological deposits, 189*A*.
- water circulating systems, effect of sulphur dioxide, 189*A*.
- wrought iron, cadmium plated, in soils, 126*A*.
- wrought iron in soils, 110*P*., 126*A*.
- zinc in chloride solutions, 226*A*.
- zinc in soils, 110*P*., 127*A*.
- zinc coatings, 226*A*.
- zinc coatings, electrolytic, 190*A*.
- CORROSION MEASUREMENTS, null method, 127*A*.
- CORROSION RESISTANCE, welded joints, 215*A*.
- CORROSION STUDIES, use of statistical control, 155*A*.
- CORROSION TESTING MACHINE, 224*A*.
- CORROSION TESTS, atmospheric, 39*A*.
- COSTS :
  - fuel, for reheating furnaces, 43*A*., 91*A*.
  - in iron industry, 47*A*.
  - open-hearth process, 51*A*.
  - open-hearth steel plants, 11*A*.
  - rolling of billets, 141*A*.
- CRACKING :
  - intercrystalline, boiler steel, 155*A*.
  - thermal, cast iron brake drums, 135*A*.
- CRACKS :
  - detection, Glo-Crack method, 217*A*.
  - detection, magnetic powder method, 218*A*.
  - fatigue, in axles, detection, 183*A*.
  - hair-line, formation, 193 *Paper*, 203 *Paper*.
  - hair-line, formation, effect of carbon, 229*P*.
  - hair-line, formation, effect of stresses, 251*P*., 253*P*.
  - hardness, in high-speed steel, 108*A*.
  - in gas cylinders, 37*A*.
  - in welded bridges, 21*A*.
- CRANKSHAFTS :
  - cast iron compared with steel, 134*A*.
  - chromium plating, 147*A*.
  - fatigue strength, 184*A*.
  - forging, 13*A*.

## CREEP :

- mechanics, 149*A*.
- steel, 149*A*.

## CREEP STRENGTH :

- columbium steel, 72*A*.
- effect of temperature, 27*A*.
- iron-columbium alloys, 72*A*.
- molybdenum steel, effect of carbon, 149*A*., 150*A*.
- vanadium steel, effect of carbon, 149*A*., 150*A*.

CREEP TESTS, boiler tubes, 28*A*.CRITICAL POINTS, determination, 222*A*.CRUCIBLES, graphite, life, 74*A*.CRUSHER CASTINGS, moulding, 101*A*.CRUSHING, iron ore, 89*A*.CUBAN CHROME ORE, plasticity, 205*A*.CUMMINGBOND, use in moulding sand, 437*P*.CUPOLA PRACTICE, 8*A*., 47*A*., 96*A*., 167*A*., 200*A*.

## CUPOLAS :

- blast control, 200*A*.
- effect of moisture and preheating blast on cast iron, 97*A*.
- mixing and rotation of charges, 134*A*.
- production of high-duty cast iron, 96*A*.

## CUTTING :

- oxy-acetylene, 21*A*., 66*A*.
- use of abrasive discs, 112*A*.

CUTTING TOOLS, performance, 22*A*., 111*A*.CYANIDE, determination in salt baths, 62*A*.CYANIDING, dry, 63*A*.CYLINDER COVERS, moulding, 168*A*.

## CYLINDER LINERS :

- chromium plating, 147*A*.
- use of cast iron, 122*A*.

## CYLINDERS :

- gas, cracking, 37*A*.
- gas, specification, British, 185*A*.

CZECHOSLOVAKIA, roasting of iron ore, 131*A*.

## DAMPING CAPACITY :

- aluminium alloys, 70*A*.
- bakelite, 70*A*.
- bronze, 70*A*.
- cast iron, 70*A*.
- cobalt, 70*A*.
- copper-zinc alloys, 70*A*.
- glass, 70*A*.
- iron-nickel alloys, 70*A*.
- ivory, 70*A*.
- ivory, 70*A*.

- DAMPING CAPACITY (*contd.*)—  
 magnesium alloys, 70A.  
 monel metal, 70A.  
 nickel, 70A.  
 steel, 70A.
- DAVIS TEST, for coking coal, 44A.
- DEAD STEEL, 147A.
- DECARBURISATION, iron, R.K. process, 7A.
- DEEP DRAWING, stainless steel, 209A.
- DEFECTS :  
 in cast iron, 75A.  
 in castings, 101A.  
 in enamel coatings on cast iron, 115A.  
 in enamel coatings on steel, effect of oxide coatings, 116A.  
 in rails and tyres, 69A.  
 in steel, 119A., 208A.
- DEGREASING, metals, 176A.
- DELAWARE, LACKAWANNA & WESTERN RAILROAD, forging plant, 58A.
- DENSENERS, use for malleable iron castings, 48A., 49A.
- DENSITOMETERS, 152A.
- DENSITY, coke, determination, 93A.
- DEOXIDATION, steel with titanium, 100A.
- DEOXIDISERS :  
 effect on free cutting steel, machinability, 148A.  
 effect on steel, 219A.
- DEPHOSPHORISATION, acid Bessemer steel, 50A.
- DESEAMING :  
 billets, 22A., 176A.  
 ingots and blooms, 23A.
- DESULPHURISATION :  
 cast iron, soda ash method, 98A.  
 pig iron, 94A.  
 pig iron, soda ash treatment, 133A.  
 steel, 52A.  
 steel, with calcium silicates, 138A.  
 steel in open-hearth process, 170A.
- DEW-POINT, gas, determination, 132A.
- DIE BLOCKS, heat treatment, 65A.
- DIES :  
 carbide, use for drawing bars, 13A.  
 drawing, carbide, 141A.  
 drawing, contour, 141A.  
 drawing, use of wood, 106A.  
 forging, design, 140A., 172A.  
 forging, inserts for, 172A.
- DIFFUSION, effect on transformation curves, 77A.
- DISTRIBOND, use in moulding sand, 431P.
- DOLOMITE. *See* Refractory Materials.
- DOMINION FOUNDRIES AND STEEL, LTD., plant, 137A.
- DOORS, water-cooled, for open-hearth furnaces, 104A.
- DRAWABILITY, thin sheets, evaluation, 58A.
- DRAWING :  
 bars, use of carbide dies, 13A.  
 deep, stainless steel, 209A.  
 shells, 140A.  
 wire, backward pull, 106A.  
 wire, formulæ for, 13A.  
 wire, heating up of metal, 172A.  
 wire, history, 13A.
- DRAWING DIES :  
 carbide, 141A.  
 contour, 141A.  
 use of wood, 106A.
- DRILLING, hardened parts, 22A.
- DRILLS :  
 Hardsteel, 22A.  
 rock, use of chromium-molybdenum steel, 73A.  
 sharpening, 212A.
- DROP FORGINGS, use in aircraft construction, 58A.
- DROP HAMMERS, elimination of vibrations, 57A.
- DROP REACTIONS, use in analysis, 157A.
- DRYING :  
 blast, 7A., 166A.  
 coal, Fleissner process, 197A.  
 moulds, use of infra-red rays, 101A.
- DUPLEX PROCESS :  
 development in America, 137A.  
 development in United States, 204A.  
 for production of chromium-nickel steel, 54A.
- DURHAM COAL, coking properties, 4A.
- DUST CATCHERS, for gas producers, 6A.
- DYNAMO STEEL, effect of cold rolling and annealing, 120A.
- ELASTIC CONSTANTS, polycrystalline iron, difference between those determined mechanically and by X-rays, 35A.
- ELASTIC PROPERTIES :  
 alloy cast iron, 31A.  
 copper, 119A.  
 nickel, 119A.  
 open-hearth iron, 119A.  
 steel, 119A.
- ELECTRIC AUTO-LITE Co., plant, 101A.

**ELECTRIC CURRENTS :**

- effect on acid attack of iron, 226A.
- use in heat treatment, 107A., 174A., 212A.

**ELECTRIC DRIVING :**

- rolling mills, 14A.
- rolling mills, use of d.c. system, 210A.

**ELECTRIC FURNACES :**

- arc, 104A., 138A., 207A.
- arc, for laboratory use, 151A.
- arc, refractory materials for, 42A., 43A.
- compared with converters, 54A.
- high-frequency, 12A.
- high-frequency, durability of basic linings, 55A.
- high-frequency, magnesite linings for, 54A., 55A.
- linings, rammed, 43A.
- refractory materials for, 90A.
- resistor, manufacture of steel, 11A.

- rotating induction, for study of slag-metal equilibria, 104A.
- slag-metal equilibria, 56A.

**ELECTRICAL INSTRUMENTS, use in rolling-mill plants, 16A.****ELECTRICAL SHEETS, magnetostriction, 70A.****ELECTRICAL TESTS, 68A.****ELECTRODEPOSITION :**

- cadmium, 113A.
- chromium, 24A., 113A.
- chromium, temperature control, 177A.
- copper, 113A.
- gold, 113A.
- lead, 24A.
- manganese, 194A.
- metals on stainless steel, 180A.
- nickel, 24A., 113A.
- nickel on irregular-shaped articles, 177A.
- rhodium, 113A.
- silver, 113A.
- tin, 24A., 113A., 114A., 182A.
- zinc, 113A.

**ELECTRODES, welding, economical use, 174A.****ELECTROGRAPHIC METHOD of analysis, 157A.****ELECTROLYTIC CLEANING, 112A.****ELECTROLYTIC POLISHING, 34A., 186A.****ELECTROLYTIC TINNING, 114A., 182A.****ELECTRON MICROSCOPES, use of surface replicas of etched metals, 221A.****ELECTROSTATIC PRECIPITATION, gases, 5A.****ELINVAR, properties, 71A.****EMMEL IRON, properties, 31A.****ENAMEL, removal from sheets, 206A.****ENAMEL COATINGS :**

- on cast iron, defects, 115A.
- defects, effect of hydrogen, 116A.
- on steel, blisters, 115A.
- on steel, effect of oxide coatings, 116A.

**ENAMELLED SHEETS, removal of enamel, 206A.****ENGINE BED-PLATES, moulding, 49A.****ENGLAND, first cast iron cannon, 131 Paper.****ENTROPY, applications, 4A.****EQUILIBRIA, heterogeneous, symbols for, 153A.****EROSION :**

- cavitation, droplet impact tests, 155A.
- cavitation, resistance of metals to, 37A.
- cavitation, vibratory tests, 155A.

**ETCHED METALS, use of surface replicas in microscopy, 221A.****ETCHING, deep, 75A.****EXCAVATING MACHINERY, for iron mines, 194A.****EXPANSION, thermal, moulding sand, 419P.****FACINGS, welded, properties, 20A.****FAILURE, gears, 147A.****FATIGUE, chafing, 184A.****FATIGUE CRACKS, in axles, detection, 183A.****FATIGUE DIAGRAMS, three dimensional, 217A.****FATIGUE STRENGTH :**

- calculation, 69A.
- crankshafts, 184A.
- effect of principal stresses, 184A.
- steel at low temperatures, 218A.
- welds, 146A.
- welds, effect of notches, 21A.

**FATIGUE TESTS, bend, welded plates, 20A.****FEEDERS, for malleable iron castings, 48A., 49A.****FERRIC - OXIDE/FERROSO - FERRIC OXIDE SYSTEM, 166A.****FERRO-CHROMIUM :**

- production in Australia, 95A.
- production in Brazil, 199A.
- production in United States, 41A.

**FERRO-MANGANESE :**

- production in Australia, 95A.
- production in Brazil, 199A.

- FERRO-SILICON :**  
     production in Australia, 95*A*.  
     production in Brazil, 199*A*.  
**FERRO-TUNGSTEN :**  
     production in Australia, 95*A*.  
     production in Brazil, 199*A*.  
**FIBROUS MATERIALS,** thermal conductivity, 90*A*.  
**FILMS :**  
     oxide, balance for studying, 225*A*.  
     oxide, on iron, 127*A*.  
     rate of formation on metals, 79*A*.  
**FIRE BRICKS.** *See* Refractory Materials.  
**FLAKES,** in steel, 53*A*.  
**FLEISSNER PROCESS,** for drying coal, 197*A*.  
**FLOW,** metal in forging, 13*A*.  
**FLUE DUST.** *See* Blast-Furnace Flue Dust.  
**FLUX,** welding, for high-sulphur steel, 215*A*.  
**FORGE FURNACES,** 105*A*., 139*A*.  
     thermal efficiency, 209*A*.  
**FORGEABILITY :**  
     copper steel, 150*A*.  
     metals, 140*A*.  
**FORGING :**  
     crankshafts, 13*A*.  
     flow of metal, 13*A*.  
     shells, 140*A*.  
     shells, "one shot" method, 12*A*.  
     shells, Witter process, 13*A*.  
     tractor parts, 172*A*.  
**FORGING DIES :**  
     design, 140*A*., 172*A*.  
     inserts for, 172*A*.  
**FORGING MACHINES,** upset, 173*A*.  
**FORGING PRACTICE,** 105*A*., 140*A*.  
**FORGING STEEL,** deoxidisers, 219*A*.  
**FORGINGS :**  
     drop, use in aircraft construction, 58*A*.  
     properties, 26*A*., 118*A*.  
**FOUNDRIES :**  
     elimination of dust and noise, 136*A*., 137*A*.  
     mechanisation, 50*A*.  
     organisation, 47*A*.  
     steel, productive capacity, 202*A*.  
**FOUNDRY PATTERNS,** use of paper, 101*A*.  
**FOUNDRY PLANT :**  
     Auto Specialities Manufacturing Co., 100*A*.  
     Electric Auto-Lite Co., 101*A*.  
     Lynchburg Foundry Co., 134*A*.  
     Ruston and Hornsby, Ltd., 95*A*.  
**FOUNDRY PRACTICE,** 8*A*., 47*A*., 95*A*., 134*A*., 167*A*., 200*A*.  
**FOUNDRY PRACTICE (contd.)—**  
     increasing production, 99*A*.  
     steel, British, 98*A*.  
**FOX, SAMUEL & Co., LTD.,** plant, 203*A*.  
**FRACTURES,** woody in steel, 35*A*.  
**FRANCE,** iron and steel industry, 137*A*.  
**FREE-CUTTING STEEL :**  
     machinability, effect of elements, 148*A*.  
     production, 51*A*., 170*A*.  
     rolling, 59*A*.  
**FUEL :**  
     costs, for reheating furnaces, 43*A*., 91*A*.  
     low-grade, use in producers, 165*A*.  
     pulverised. *See* Coal, pulverised.  
**FUEL DEPARTMENT,** organisation, 163*A*.  
**FUEL ECONOMY,** in iron and steel industry, 91*A*., 163*A*.  
**FULBOND,** use in moulding sand, 424*P*.  
**FULLERS' EARTH,** use in moulding sand, 422*P*.  
**FURNACES :**  
     blast. *See* Blast Furnaces.  
     electric. *See* Electric Furnaces.  
     forge. *See* Forge Furnaces.  
     heat transfer, 4*A*.  
     heat-treatment. *See* Heat-Treatment Furnaces, Annealing Furnaces, &c.  
     malleable iron. *See* Malleable Iron Furnaces.  
     metallurgical, mechanical stokers for, 43*A*.  
     open-hearth. *See* Open-Hearth Furnaces.  
     regenerative, fuel-rate control, Brown system, 206*A*.  
     reheating. *See* Reheating Furnaces and Soaking Pits.  
     rotary, linings, materials for, 63*P*., 67*P*.  
     rotary, linings, patching process, 66*P*.  
     rotary, production of steel castings, 53 *Paper*.  
     rotary, reduction of iron ore, 133*A*.  
**FUSAIN,** determination in coal, 158*A*.  
**GALVANISED STEEL,** corrosion in soils, 126*A*.  
**GALVANISED VESSELS,** corrosion by pig food, 192*A*.  
**GALVANISING,** 24*A*.



GALVANISING (*contd.*)—

- effect of alloying elements in bath, 181A.
- heat requirements, 114A.
- welded joints, 181A.

## GAS :

- blast-furnace. *See* Blast-Furnace Gas.
- cleaning, electrostatic precipitation, 5A.
- coke-oven. *See* Coke-Oven Gas.
- dew-point, determination, 132A.
- flue, determination of sulphur dioxide, 83A.
- long-distance, use in reheating furnaces, 105A.

## GAS CYLINDERS :

- cracking, 37A.
- specification, British, 185A.

GAS PRODUCERS. *See* Producers.

## GASES :

- evolved from core sands, 446P.
- in acid open-hearth steel, 206A.
- in liquid steel, 52A.
- in liquid steel, analysis, 80A.

## GATING, castings, 49A.

## GAUGES :

- chromium plating, 147A.
- for determining thickness, 16A.
- pressure, 16A.
- strain, 16A.

## GEAR TEETH, quenching after tempering, 183A.

## GEAR WHEELS, moulding, 168A.

## GEARS :

- case-hardening, 62A.
- failure, 147A.
- heat treatment, 173A.
- manufacture from iron powder, 46A., 200A.
- selection of case-hardening steels for, 16A.

## GENERAL ELECTRIC Co., production of magnets, 148A.

## GÉNÉRAL MOTORS CORPORATION, use of clay slurry in moulding sand, 136A.

## GIESELER TEST, for coking coal, 44A., 165A.

## GLASS, damping capacity, 70A.

## GLO-CRACK METHOD, of detecting cracks, 217A.

## GLOSSARY, terms used in powder metallurgy, 8A.

## GOLD, electrodeposition, 113A.

## GRAIN GROWTH, effect of capillarity in grain boundaries, 36A.

## GRAIN SIZE, determination, 124A.

## GRANULAR MATERIALS, thermal conductivity, 90A.

## GRAPHITE :

- amorphous, recarburisation of open-hearth steel, 52A.
- solubility in austenite, 186A.
- thermal conductivity, 91A.

## GRAPHITISATION :

- cast iron, effect of silicon and nickel, 101A.
- chilled castings, 102A.

## GRAY-KING TEST for coal, 164A.

## GREASES, use for rust prevention, 188A.

## GREAT LAKES STEEL CORP. :

- fuel oil supply system, 206A.
- sintering plant, 195A.

## GREENAWALT SINTERING PLANT, at Julienhütte, 2A.

## GROWTH, cast iron, effect of aluminium coatings, 182A.

## GUILLEMIN EFFECT, 70A.

## GUNS, centrifugal casting, 49A.

## HAIR-LINE CRACKS :

- formation, 193 *Paper*, 203 *Paper*.
- formation, effect of carbon, 229P.
- formation, effect of stresses, 251P., 253P.

## HARDENABILITY :

- carbon steel, 16A.
- chromium - molybdenum - nickel steel, 16A.
- steel, 69A., 219A.

## HARDENABILITY TESTS :

- chromium - molybdenum - nickel steel, 148A.
- molybdenum steel, 148A.

## HARDENED PARTS, drilling, 22A.

## HARDENING :

- flame, 143A., 213A.
- flame, cylindrical surfaces, 213A.
- flame, rails, 62A.
- high-speed steel, 107A.
- induction, 107A., 174A., 212A.
- precipitation, iron-columbium alloys, 72A.
- selective, 62A.

## HARDNESS, weld metal, effect of composition, 175A.

## HARDNESS CRACKS, in high-speed steel, 108A.

## HARDNESS TESTS :

- for determining tensile strength, 218A.
- scatter in, 120A.

## HARDSTEEL DRILLS, 22A.

## HEAT :

- consumption per ton of metallic charge in open-hearth practice, 51A.

**HEAT (contd.)—**

- radiant, use for heat-treatment furnaces, 61A.
- requirements of basic Bessemer and open-hearth processes, 52A.
- requirements in galvanising, 114A.
- HEAT BALANCES**, ore sintering plants, 89A.
- HEAT EXCHANGERS**, corrosion, use of inhibitors and their effect on heat transfer, 73P.
- HEAT-RESISTANT STEEL** :
  - properties, 123A.
  - scaling, 17A., 63A.
- HEAT TRANSFER** :
  - effect of corrosion inhibitors, 73P.
  - furnaces, 4A.
- HEAT TREATMENT**, 16A., 61A., 106A., 143A., 173A., 211A.
  - bolts and nuts, 18A.
  - chromium - cobalt - molybdenum - nickel steel, 151A.
  - chromium - columbium - nickel - titanium steel, 151A.
  - chromium-manganese steel, 151A.
  - chromium - molybdenum - nickel steel, 65A., 151A.
  - chromium-nickel steel, 151A.
  - die blocks, 65A.
  - effect on iron-aluminium-nickel alloys, 78A., 224A.
  - effect on steel, 117A.
  - gears, 173A.
  - high-speed steel, 143A.
  - lifting jacks, 173A.
  - molybdenum high-speed steel, 16A.
  - pump parts, 108A.
  - shells, 107A.
  - tool-steel, 212A.
  - use of electric currents, 107A., 174A., 212A.
  - use of salt baths, 17A., 143A., 173A., 212A.
  - use of salt baths, cyanide determination, 62A.
  - use of salt baths, position and shape of electrodes, 107A.
  - wire, 62A.
- HEAT-TREATMENT FURNACES** :
  - for aircraft parts, 173A.
  - for bombs, 18A.
  - Catenary type, 18A.
  - controlled atmospheres, 61A., 107A., 173A., 211A.
  - electric, 18A., 61A., 106A.
  - gas-fired, 106A.
  - radiant heat, 61A.
- HEMATITE-MAGNETITE SYSTEM**, 166A.
- HIGH-FREQUENCY FURNACES**. *See* Electric Furnaces.

**HIGH-SPEED STEEL :**

- austenite transformation, 76A.
- chromium-vanadium, effect of molybdenum and titanium, 31A.
- hardening, 107A.
- hardness cracks, 108A.
- heat treatment, 143A.
- molybdenum, heat treatment, 16A.
- molybdenum, properties, 73A., 122A.
- nitriding, 63A.
- properties, 22A.
- quenching, 76A.
- HIGH-SPEED STEEL INGOTS**, heterogeneity, 207A.
- HIGH-SPEED STEEL TIPS**, fixed to carbon steel shanks, 111A., 145A.
- HISTORY** :
  - cast iron cannon in England, 131 *Paper*.
  - slitting mills, 15A.
  - wire drawing, 13A.
- HYDRAULIC PLANTS** :
  - use of compressed air in, at Bessemer works, 57A.
  - use in steelworks, 57A.
- HYDROCHLORIC ACID** :
  - corrosion of alloys, 125A.
  - corrosion of steel, 191A.
  - effect on stainless steel, corrosion-resistance, 127A.
- HYDROGEN** :
  - calculation of amount in blast-furnace gas, 45A.
  - effect in cast iron, 72A.
  - effect in enamel coatings, 116A.
  - effect in malleable cast iron, annealing time, 167A.
  - effect in steel, 72A.
  - effect in steel, brittleness, 30A.
  - effect in steel, hair-line crack formation, 193P., 203P.
  - evolution from steel, 205P.
  - in liquid steel, 52A.
  - reduction of iron ore, 200A.
  - solubility in iron and iron alloys, 181 *Paper*.
  - solubility in iron-nickel alloys, 181P.
  - solubility in nickel steel, 181P.
- IDAHO**, tungsten ore deposits, 87A.
- IGNITION RECTIFIERS**, for rolling-mill motors, 141A.
- ILLINOIS COAL**, determination of fusain, 158A.
- IMPACT STRENGTH**, spot welds, 65A.

INCLUSIONS, spectrum analysis, 81A.  
 INFRA-RED RAYS, use for drying moulds, 101A.  
 INGOT IRON, corrosion in soil, 110P.  
 INGOT MOULDS :  
   cast iron stools for, 56A., 206A.  
   stools for, 207A.  
   for tool steel, 56A.  
   washes for, 207A.  
 INGOTS :  
   deseaming, 23A.  
   high-speed steel, heterogeneity, 207A.  
   rimming steel, Bessemer, manufacture and composition, 295 *Paper*, 327 *Paper*.  
   rimming steel, open-hearth, composition variation from outside to centre, 345 *Paper*.  
   rimming steel, open-hearth, manufacture and composition, 283 *Paper*.  
   sound, production, 56A.  
 INHIBITORS, effect on corrosion and heat transfer in heat exchangers, 73P.  
 INOCULATED IRON, properties, 31A.  
 INSULATING BRICKS, thermal conductivity, 90A.  
 INTENSIFYING SCREENS for radiographs, 76A.  
 INTERMETALLIC PHASES, linking, 153A.  
 INTERNATIONAL HARVESTER Co., forging plant, 172A.  
 IODINE, recovery from flue dust, 199A.  
 IRON :  
   corrosion in acids, effect of electric currents, 226A.  
   corrosion, atmospheric, 187A.  
   corrosion in chloride solutions, 226A.  
   crystal structure, 157P.  
   determination, Moore's electrolytic method, 157A.  
   effect in galvanising bath on coatings, 181A.  
   high-sulphur, effect of calcium, 37A.  
   liquid, absorption of nitrogen, 30A.  
   liquid, carbon-oxygen equilibrium, 205A.  
   open-hearth, elastic properties, 119A.  
   oxide films, 127A.  
   passive, activation in nitric acid, 190A.  
   polycrystalline, elastic constants, difference between those determined mechanically and by X-rays, 35A.

IRON (*contd.*)—  
   production, 7A., 45A., 94A., 133A., 166A., 198A.  
   pure, properties, 183A.  
   reaction with steam, 225A.  
   silicon, magnetisation near boundaries, 120A.  
   solubility of hydrogen, 181 *Paper*.  
 IRON ALLOYS, solubility of hydrogen, 181 *Paper*.  
 IRON - ALUMINIUM - COBALT - NICKEL ALLOYS, use for magnets, 148A.  
 IRON-ALUMINIUM-NICKEL ALLOYS :  
   effect of heat treatment, 78A., 224A.  
   sintered, use for magnets, 46A.  
 IRON-ALUMINIUM-NICKEL DIAGRAM, 77A.  
 IRON/CALCIUM-SULPHIDE SYSTEM, 36A.  
 IRON CARBIDE, isolation, electrolytic method, 35A., 222A.  
 IRON-CARBON ALLOYS, absorption of nitrogen, 30A.  
 IRON-CHROMIUM ALLOYS, absorption of nitrogen, 30A.  
 IRON COBALT ALLOYS, corrosion, 125A.  
 IRON-COLUMBIUM ALLOYS, precipitation hardening and creep strength, 72A.  
 IRON INDUSTRY :  
   French, 137A.  
   Japan, 46A.  
 IRON/IRON-SULPHIDE/CALCIUM-SULPHIDE SYSTEM, 36A.  
 IRON-MANGANESE ALLOYS, corrosion, 125A.  
 IRON MINES, excavating machinery, 194A.  
 IRON-NICKEL ALLOYS :  
   corrosion, 125A.  
   damping capacity, 70A.  
   solubility of hydrogen, 181P.  
 IRON ORE :  
   analysis, Moore's electrolytic method, 157A.  
   for basic open-hearth process, 204A.  
   briquetting, 206A.  
   concentration, 2A.  
   crushing, 89A.  
   determination of phosphorus, 158A.  
   low-grade, preparation, 89A.  
   manganiferous, concentration, 88A.  
   manganiferous, leaching, 194A.  
   microstructure, radiographic method of study, 76A.  
   Minette, sintering, 195A.  
   Minette, smelting, 195A.

**IRON ORE (contd.)—**

- mining in Lincolnshire, 194A.
- mining in Minnesota, 194A.
- mixing, 89A.
- reduction with hydrogen, 200A.
- reduction in rotary furnaces, 133A.
- roasting in Czechoslovakia, 131A.
- roasting in Poland, 131A.
- sintering, 2A., 195A., 206A.
- sintering plants, heat balances, 89A.

**IRON ORE DEPOSITS :**

- Japan, 1A., 87A.
- Korea, 1A.
- South America, 87A.

**IRON-ORE INDUSTRY, United States, 2A.****IRON-ORE RESOURCES, Manchukuo, 1A.****IRON OXIDE :**

- effect on carbon monoxide, decomposition, 3A.
- effect on methane, decomposition, 3A.
- effect of other oxides at high temperatures, 198A.

**IRON-OXYGEN SYSTEM, 159P.****IRON-PHOSPHORUS ALLOYS, absorption of nitrogen, 30A.****IRON POWDERS. See Powdered Iron.****IRON-SILICON ALLOYS, acid-resistant, manufacture, 133A.****IRON-ZINC COUPLES, potential changes, 38A.****IVORINE, damping capacity, 70A.****IVORY, damping capacity, 70A.****JACKS, lifting, heat treatment, 173A.****JAPAN :**

- iron industry, 46A.
- iron and steel production, 1A., 88A.
- mineral resources, 1A., 87A.

**JESSOP METHOD for production of clad steel, 113A.****JONES AND LAUGHLIN STEEL CORP., drying of blast, 166A.****JOULE EFFECT, 70A.****JULENHÜTTE, Greenawalt sintering plant, 2A.****KOPPERS-BECKER COKE OVEN, heating, 92A.****KOREA, mineral resources, 1A., 88A.****KRUPP-RENN PROCESS, 200A.****LABORATORIES, arc furnaces for, 151A.****LADLES :**

- drying and preheating, 47A.
- nozzle-cap, bricks for, 205A.
- two-nozzle, 207A.

**LALANCE & GROSJEAN MFG. Co., plant, 209A.****LATTICE DISTORTION, X-ray investigation, 152A.****LATTICE RELATIONSHIP, austenite decomposition products, 223A.****LEACHING :**

- manganese ore, 41A.
- manganiferous iron ore, 194A.

**LEAD :**

- corrosion in soils, 127A.
- effect in galvanising bath on coatings, 181A.
- electrodeposition, 24A.

**LEAD ORE, concentration, 89A.****LECO APPARATUS, use in analysis, 205A.****LESSING TEST, for coal, 164A.****LEVELLING MACHINES for sheets and strip, 59A.****LIME, burnt, effect on carbon monoxide, decomposition, 3A.****LIME-ALUMINA-SILICA SYSTEM, 33P.****LIME-SILICA-MAGNESIA SYSTEM, 35P.****LINCOLNSHIRE, iron-ore mining, 194A.****LININGS :**

- basic open-hearth tilting furnaces, 9 Paper.
- blast-furnace, wear, 162A.
- electric furnace, ramming, 43A.
- Sesci furnaces, materials for, 63P., 67P.
- Sesci furnaces, patching process, 66P.

**LUBRICANTS :**

- filtration and reclamation, 210A.
- high load-carrying capacity, 210A.

**LUBRICATION, strip mills, 14A.****LYNCHBURG FOUNDRY Co., plant, 134A.****MACHINABILITY :**

- cast iron, effect of elements, 148A.
- free-cutting steel, effect of elements, 148A.
- malleable cast iron, 148A.
- steel, effect of elements, 27A., 148A.

**MACHINING, metals, 22A., 111A.****MACROGRAPHIC EXAMINATION, metals, 34A.****MAGNESIA-SILICA SYSTEM, 196A.****MAGNESITE. See Refractory Materials.**



- MAGNESIUM, oxide coatings, 114A.  
 MAGNESIUM ALLOYS, damping capacity, 70A.  
 MAGNESIUM CHROMATE, use as corrosion inhibitor, 73P.  
 MAGNETIC POWDER METHOD of detecting cracks, 218A.  
 MAGNETIC TESTS, 68A.  
 MAGNETISATION, metals near boundaries, 120A.  
 MAGNETITE, crystal structure, 157P.  
 MAGNETOSTRICTION, silicon steel, 70A.  
 MAGNETOSTRICTION PHENOMENA, 70A.  
 MAGNETS :  
   permanent, production, 148A.  
   production from sintered iron-aluminium-nickel alloys, 46A.  
   use of cold-worked manganese steel, 27A., 149A.  
 MAGNITOGORSK WORKS, blowing-out of blast-furnace, 45A.  
 MAGNO, 179A.  
 MAINS, hot-blast, design, 198A.  
 MALLEABLE CAST IRON :  
   annealing time, effect of hydrogen, 167A.  
   behaviour in molten zinc, 181A.  
   corrosion in soils, 126A.  
   machinability, 148A.  
   short-time annealing, 98A.  
   shrinkage and contraction, 48A.  
 MALLEABLE IRON CASTINGS :  
   feeders for, 48A., 49A.  
   production, 49A.  
   use of denseners, 48A., 49A.  
 MALLEABLE IRON FURNACES, refractory materials for, 90A.  
 MANCHUKUO, mineral resources, 1A., 88A.  
 MANGANESE :  
   determination in iron and steel, 82A., 157A.  
   determination in pig iron, 82A.  
   effect on calcium silicates, desulphurising power, 138A.  
   effect in cast iron, 151A.  
   effect in cast iron, austenite transformation, 187A.  
   effect in cast iron, machinability, 148A.  
   effect in free-cutting steel, machinability, 148A.  
   effect in steel, machinability, 27A., 148A.  
   effect in structural steel, brittleness, 32A.  
   electrodeposition, 194A.  
   recovery, nitrogen dioxide process, 88A.  
 MANGANESE-MOLYBDENUM STEEL, effect of tin, 141P.  
 MANGANESE ORE :  
   concentration, 41A., 88A., 89A., 131A., 194A.  
   leaching, 41A.  
   nodulising, 88A.  
   sintering, 88A.  
 MANGANESE ORE DEPOSITS :  
   Arkansas, 87A.  
   Japan, 1A.  
   Korea, 1A.  
   Manchukuo, 1A.  
   Montana, 1A.  
   New Mexico, 1A.  
   South America, 87A.  
   United States, 1A.  
 MANGANESE STEEL :  
   cold-worked, use for magnets, 27A., 149A.  
   weldability tests, 20A.  
 MANGANESE-STEEL CASTINGS, properties, 220A.  
 MANGANESE-STEEL GAS CYLINDERS, specification, British, 185A.  
 MANGANESE-VANADIUM STEEL, production, 171A.  
 MANGANIC OXIDE, effect on iron oxide at high temperatures, 199A.  
 MANGANIFEROUS IRON ORE :  
   concentration, 88A.  
   leaching, 194A.  
 MARTENSITE, lattice relationship to austenite, 223A.  
 MAURER'S DIAGRAM for cast iron, 67A.  
 MEEHANITE :  
   for cylinder covers, 168A.  
   properties, 31A.  
   thermal cracking, 135A.  
   use for crankshafts, 134A.  
 MEMBERS, election, 2P.  
 MERCURY ORE, concentration, 89A.  
 METALLOGRAPHIC POLISHING, cast iron, 124A.  
 METALLOGRAPHIC SPECIMENS, storage, 186A.  
 METALLOGRAPHY, development, 74A.  
 METALLOGRAPHY AND CONSTITUTION, 34A., 74A., 124A., 152A., 186A., 221A.  
 METALLURGISTS, training, 124A., 221A.  
 METHANE, decomposition, catalytic effect of metals and oxides, 3A.  
 MICA, thermal conductivity, 90A.  
 MICROBIOLOGICAL DEPOSITS :  
   formation in water-circulating systems, 189A.  
   formation in water-circulating systems, bibliography, 189A.

MICROPHOTOMETERS, 152*A*.  
 MICROSCOPE, electron, use of surface replicas of etched metals, 221*A*.  
 MICROSCOPIC EXAMINATION :  
   metals, 124*A*.  
   ore minerals, 34*A*.  
 MICROSTRUCTURE, iron ore, radio-graphic method of study, 76*A*.  
 MINERAL RESOURCES, 1*A*., 87*A*.  
 MINETTE ORE :  
   sintering, 195*A*.  
   smelting, 195*A*.  
 MINING :  
   iron ore, Lincolnshire, 194*A*.  
   iron ore, Minnesota, 194*A*.  
 MINNESOTA, iron-ore mining, 194*A*.  
 MIXER PRACTICE, English and American, 206*A*.  
 MIXING, iron ore, 89*A*.  
 MOLYBDENUM :  
   determination in iron and steel, 157*A*.  
   determination, use of photo-electric colorimeter, 205*A*.  
   effect in cast iron, 31*A*.  
   effect in cast iron, austenite transformation, 187*A*.  
   effect in cast iron, machinability, 148*A*.  
   effect in chromium-vanadium steel, 31*A*.  
   effect in structural steel, brittleness, 32*A*.  
 MOLYBDENUM CAST IRON, thermal cracking, 135*A*.  
 MOLYBDENUM HIGH-SPEED STEEL :  
   heat-treatment, 16*A*.  
   properties, 73*A*., 122*A*.  
 MOLYBDENUM-NICKEL CAST IRON, production, 48*A*.  
 MOLYBDENUM ORE DEPOSITS, South America, 87*A*.  
 MOLYBDENUM STEEL :  
   creep strength, effect of carbon, 149*A*., 150*A*.  
   hardenability tests, 148*A*.  
 MOLYBDENUM-STEEL CASTINGS, properties, 220*A*.  
 MOLYBDENUM TOOL STEEL, properties, 144*A*.  
 MONEL METAL, damping capacity, 70*A*.  
 MONTANA :  
   chromium ore deposits, 1*A*.  
   manganese ore deposits, 1*A*.  
 MOORE'S METHOD for determination of iron, 157*A*.  
 MORTARS, production, 100*A*.

MOULDING :  
   anchors, 202*A*.  
   bombs, 136*A*.  
   crusher casting, 101*A*.  
   cylinder covers, 168*A*.  
   engine bed-plate, 49*A*.  
   gear wheels, 168*A*.  
   large iron castings, 202*A*.  
   pipe fittings, 134*A*.  
   plough parts, 134*A*.  
   rolls, 10*A*.  
   shells, 49*A*.  
   strickle, 101*A*.  
 MOULDING SAND :  
   addition of clay slurry, 136*A*.  
   bonding materials, 423*P*., 428*P*.  
   British, composition and properties, 396*P*.  
   effect of milling, 409*P*.  
   effect of surface-tension-reducing agents, 413*P*.  
   mixing, 9*A*.  
   nature of clay substances, 100*A*.  
   permeability, 414*P*.  
   permeability tests, apparatus, 416*P*.  
   reclamation, 9*A*.  
   report of Sub-Committee, 393 *Paper*.  
   tests, 48*A*., 100*A*., 136*A*.  
   thermal conductivity of insulating mixtures, 420*P*.  
   thermal expansion of sand-clay mixtures, 419*P*.  
   use of Beacon bentonite substitute, 436*P*.  
   use of Benbond, 430*P*.  
   use of bentonite, 423*P*.  
   use of clay, 428*P*.  
   use of Colbond, 429*P*.  
   use of Cummingbond, 437*P*.  
   use of Distribond, 431*P*.  
   use of fullers' earth, 422*P*.  
   use of Perminal, 413*P*.  
   use of Seconite, 436*P*.  
   use of Silklay, 436*P*.  
   use of Siolite, 436*P*.  
 MOULDS :  
   drying, use of infra-red rays, 101*A*.  
   for plastics, steels used, 122*A*.  
 N.A.X. HIGH-TENSILE STEEL, welding, 144*A*., 215*A*.  
 NAGAOKA-HONDA EFFECT, 70*A*.  
 NAILS, from St. Pierre, examination, 80*A*., 154*A*.  
 NATIONAL EMERGENCY STEELS, properties, 216*A*.  
 NEW JERSEY, mineral resources, 87*A*.

## NEW MEXICO :

- manganese ore deposits, 1A.
- tin ore deposits, 1A.

## NICARB PROCESS of case-hardening, 63A.

## NICKEL :

- damping capacity, 70A.
- determination in alloy steel, 82A.
- determination in iron and steel, 158A.
- determination, use of photo-electric colorimeter, 205A.
- effect in cast iron, 31A.
- effect in cast iron, austenite transformation, 187A.
- effect in cast iron, graphitisation, 101A.
- effect in cast iron, machinability, 148A.
- effect in structural steel, brittleness, 32A.
- elastic properties, 119A.
- electrodeposition, 24A., 113A.
- electrodeposition, on irregular-shaped articles, 177A.
- magnetisation near boundaries, 120A.

## NICKEL CAST IRON :

- effect of moisture and preheating of cupola blast, 97A.
- structure, 223A.

## NICKEL COATINGS, thickness determination, 177A.

## NICKEL ORE DEPOSITS, South American, 87A.

## NICKEL-PLATING SOLUTIONS, analysis, 228A.

## NICKEL STEEL :

- effect of tin, 141P.
- pickling, 112A.
- solubility of hydrogen, 181P.
- structure, 223A.
- transformations, 77A.

## NICKEL STEEL CASTINGS :

- lowering of nickel content, 33A.
- properties, 220A.

## NICKEL STEEL PLATES, welded, stresses, effect of preheating, 145A.

NIOBIUM. *See* Columbium.

## NI-TENSILE, properties, 31A.

## NITRIC ACID :

- activation of passive iron, 190A.
- corrosion of alloys, 125A.
- corrosion of chromium-nickel steel, 192A.
- corrosion of steel, 191A.

## NITRIC ACID PLANTS, use of stainless steel, 151A.

## NITRIDING :

- chromium-molybdenum steel, 63A.
- high-speed steel, 63A.
- tank parts, 63A.

## NITRO-CEMENTATION, 63A.

## NITROGEN :

- absorption by iron and iron alloys, 30A.
- absorption by steel, 206A.
- determination in iron and steel, 80A.
- determination, use of photo-electric colorimeter, 205A.
- effect in chromium-nickel steel, 121A.
- effect in chromium steel, 121A.

## NITROGEN-DIOXIDE PROCESS for recovery of manganese ore, 88A.

## NODULISING, manganese ore, 88A.

## NOTCHES, effect on welds, fatigue strength, 21A.

## NULL METHOD of corrosion measurements, 127A.

## NUTS, heat treatment, 18A.

## OBITUARY NOTICES, deceased Members, 489P.

## OIL, use for rust prevention, 188A.

## OIL FUEL, supply system of Great Lakes Steel Corporation, 206A.

## OIL-WELL PUMPS, heat treatment, 108A.

## OPEN-HEARTH FURNACES :

- acid, refractory materials, for, 162A.
- basic, tilting, brick consumption, 16P.
- basic, tilting, linings, 9 *Paper*.
- bottoms, ramming with Ramix and Plastic K.N., 204A.
- bottoms, repair, 207A.
- bottoms, use of StaSet, 205A.
- doors, water-cooled, 104A.
- ports, water-cooled, 104A.
- repair, 205A.
- use of coke-oven gas, 207A.
- use of magnesite refractories, 42A.
- valves, Reiner, 11A.

## OPEN-HEARTH IRON, elastic properties, 119A.

## OPEN-HEARTH PERSONNEL, training, 204A.

## OPEN-HEARTH PRACTICE :

- acid, 104A., 204A.
- acid, carbon control, 206A.
- acid, slag control, 206A.
- acid, use of light scrap, 206A.
- American, 50A.
- Australian, 206A.

**OPEN-HEARTH PRACTICE (contd.)—**

- basic, 103A., 204A.
- basic, slag control, 204A.
- basic, use of blown metal, 206A.
- effect of proportion of hot-metal charge on speed of operation, 51A.
- heat consumed per ton of metallic charge, 51A.
- pig-ore process, 205A.
- recarburisation of charge with amorphous graphite, 52A.
- scrap and pig charges, 169A.
- use of soft ore, 206A.
- OPEN-HEARTH PROCESS :**
  - basic, heat requirements, 52A.
  - basic, iron ores for, 204A.
  - costs, 51A.
  - desulphurising reactions, 170A.
  - effect of increasing proportion of hot metal in charge, 205A.
- OPEN-HEARTH STEEL**, acid, gases in, 206A.
- OPEN-HEARTH STEEL PLANTS**, cost, 11A.
- ORE BRIDGES**, design, 2A.
- ORE MINERALS**, microscopic examination, 34A.
- OREGON**, chromium ore deposits, 1A.
- ORES**, mining and treatment, 2A., 41A., 88A., 131A., 194A.
- OSTWALD-LILLIE METHOD** of nerve conduction, 190A.
- OVER-HEATING**, steel, 106A.
- OXIDATION :**
  - metals, 128A., 224A.
  - steel, 157P.
- See also* Scaling.
- OXIDE COATINGS :**
  - on aluminium, 114A.
  - on iron and steel, 114A.
  - on magnesium, 114A.
  - protective value, 192A.
  - on steel, salt-spray test, 154A.
  - on zinc, 114A.
- OXIDE FILMS :**
  - balance for studying, 225A.
  - on iron, 127A.
  - removal by heating in vacuum, 213A.
- OVIFAK IRON**, corrosion, 225A.
- PAINT**, priming, specification, British, 182A.
- PAINT COATINGS :**
  - on steel, 182A.
  - substitute for zinc coatings, 117A.
- PAINTING**, precleaning of steel, 23A.

- PAPER**, use for foundry patterns, 101A.
- PARCO-LUBRITE TREATMENT** for steel, 114A.
- PASSIVE IRON**, activation in nitric acid, 190A.
- PATENTING**, wire, use of salt baths, 210A.
- PATTERNS**, foundry, use of paper, 101A.
- PEARLITE**, lattice relationships to austenite, 223A.
- PENNSYLVANIA :**
  - coal deposits, 1A.
  - mineral resources, 87A.
- PERICLASE**, conversion of magnesite, 131A.
- PERMEABILITY**, moulding sand, 414P.
- PERMEABILITY TESTS**, moulding sands, apparatus, 416P.
- PERMINAL**, use in moulding sand, 413P.
- PHASES**, intermetallic, linking, 153A.
- PHOSPHATE COATINGS**, 177A., 178A., 179A.
  - on condenser tubes, 179A.
  - on piston rings, 180A.
  - protective value, 192A., 224A.
  - sprayed, 180A.
  - on steel, 114A.
  - on steel prior to cold-work, 180A.
- PHOSPHORUS :**
  - determination in iron ore, 158A.
  - determination in pig iron, 82A.
  - determination in steel, 467P.
  - determination, use of photo-electric colorimeter, 205A.
  - effect in Bessemer steel, 122A.
  - effect in cast iron, austenite transformation, 187A.
  - effect in cast iron, machinability, 148A.
  - effect in steel, machinability, 27A.
  - effect in structural steel, brittleness, 32A.
- PHOSPHORUS PRINTS**, production, 75A.
- PHOTO-ELECTRIC ABSORPTIOMETER**, Spekker, use in analysis, 227A.
- PHOTOLUMETER**, use in analysis, 205A.
- PHOTOMETRIC METHOD** of analysis, 82A.
- PHOTOMICROGRAPHY**, 34A.
- PICKLING :**
  - cathodic, 23A.
  - chromium steel, 112A.
  - effect on corrosion of metals in soil, 115P.
  - nickel steel, 112A.
  - steel, 176A.



PICKLING LIQUOR, utilisation, 112A.  
 PIG FOOD, corrosion of galvanised vessels, 192A.

PIG IRON :  
   analysis, 82A.  
   desiliconising, 2A.  
   desulphurisation, 94A.  
   desulphurisation, soda ash treatment, 133A.

PIGMENTS, Thermocolor, for measurement of temperatures, 142A.

PIPE FITTINGS, moulding, 134A.

PIPES :  
   boiler, specification, British, 152A.  
   corrosion in soils, 38A., 126A.

PISTON RINGS, phosphate coatings, 180A.

PLASTIC K.N. for open-hearth bottoms, 204A.

PLASTICS, moulding, use of steel, 172A.

PLASTICS INDUSTRY, steel for, 122A.

PLATE MILLS, electric driving, 14A.

PLATES :  
   boiler, recrystallisation during hot working, 68A.

  welded, bend-fatigue tests, 20A.

PLOUGH PARTS, moulding, 134A.

POLAND, roasting of iron ore, 131A.

POLAROGRAPH, use in analysis, 83A., 158A., 228A.

POLISHING :  
   electrolytic, 34A., 186A.  
   metallographic, cast iron, 124A.

POROSITY :  
   in castings, 49A.  
   coke, determination, 93A.

PORTS, water-cooled, for open-hearth furnaces, 104A.

POTASSIUM CHLORIDE, recovery from flue dust, 199A.

POTASSIUM CHROMATE, use as corrosion inhibitor, 73P.

POWDER METALLURGY, 8A., 46A.  
   terms used, 8A.

POWDERED IRON :  
   manufacture of gears and bushes, 46A.  
   production of gears, 200A.  
   sintering, 95A.

PRECIPITATION HARDENING, iron-columbium alloys, 72A.

PRESSES :  
   hydraulic, 58A.  
   toggle-actuated, 209A.

PRESSING, metals, 13A.

PRESSURE GAUGES, 16A.

PRESSURE TESTS, boiler tubes, 28A.

PRESSURE VESSELS, stainless steel, welding, 175A.

## PRODUCERS :

  dust-catchers for, 6A.

  use of low-grade fuel, 165A.

  use of low-temperature coke, 196A.

PULVERISED COAL. *See* Coal, pulverised.

PUMP PARTS, heat treatment, 108A.

PYROMETRY, 60A., 142A.

*See also* Thermometers and Thermocouples.

## QUENCHING :

  high-speed steel, 76A.

  gear-wheel teeth, after tempering, 183A.

  steel, 19A., 117A.

RADIANT HEAT, use for heat-treatment furnaces, 61A.

RADIOGRAPHIC METHOD of studying microstructure of iron ore, 76A.

RADIOGRAPHS, intensifying screens for, 76A.

## RAILS :

  defects, 69A.

  flame hardening, 62A.

  heat-treated, use, 220A.

  sorbic treatment, Sandberg process, 221A.

RAMIX for open-hearth bottoms, 204A.

RECALESCENCE POINTS, determination, 222A.

RECARBURISATION, steel in open-hearth practice with amorphous graphite, 52A.

## RECRYSTALLISATION :

  boiler plate during hot working, 68A.

  silicon ferrite, 223A.

RECTIFIERS, Ignitron, for rolling-mill motors, 141A.

REELING, strip, speed and tension control, 59A.

REFRACTORY MATERIALS, 3A., 42A., 89A., 131A., 162A., 195A.

  action of slag, 162A., 196A.

  consumption in tilting furnaces, 16P.

  for blast-furnaces, 90A.

  effect of decomposition of carbon monoxide and methane, 3A.

  for electric furnaces, 90A.

  heat-treatment, 162A.

  for malleable iron furnaces, 90A.

  for open-hearth furnaces, 162A.

  thermal conductivity, 90A.

  use in arc furnaces, 42A., 43A.

- REFRACTORY MATERIALS (CARBON BLOCKS) for blast-furnace hearths, 162A.
- REFRACTORY MATERIALS (CHROME-MAGNESITE BRICKS), use in arc furnaces, 43A.
- REFRACTORY MATERIALS (CHROME ORE), properties, 42A.
- REFRACTORY MATERIALS (CHROMITE), from Shetland, properties, 89A.
- REFRACTORY MATERIALS (DOLOMITE), use for arc-furnace hearths, 43A.
- REFRACTORY MATERIALS (FIRECLAY BRICKS), manufacture and properties, 3A.
- REFRACTORY MATERIALS (MAGNESITE):  
     conversion to periclase, 131A.  
     for high-frequency furnaces, 54A., 55A.  
     use in open-hearth furnaces, 42A.
- REFRACTORY MATERIALS (SILICA BRICKS):  
     action of slag, 89A.  
     use for arc-furnace roofs, 42A., 43A.
- REFRACTORY MATERIALS (SILICON-CARBIDE BRICKS), properties, 195A.
- REHEATING FURNACES, 105A., 139A., 209A.  
     for blooms and billets, 209A.  
     design, 105A.  
     fuel cost standards, 43A., 91A.  
     use of long-distance gas, 105A.  
     use of pulverised coal, 132A.
- REINER VALUE, 11A.
- RESIDUAL METALS, in steel, 169A.
- RESISTOR FURNACES. *See* Electric Furnaces.
- RHODIUM, electrodeposition, 113A.
- RIMMING STEEL:  
     Bessemer, manufacture and composition, 295 *Paper*, 327 *Paper*.  
     carbon diffusion, 357 *Paper*.  
     open-hearth, carbon content of core, 289P.  
     open-hearth, composition variation from outside to centre, 345 *Paper*.  
     open-hearth, manufacture and composition, 283 *Paper*.  
     open-hearth sulphides in, 288P.  
     "Riss" definition, 119A.
- RIVETS, properties, 151A.
- R.K. PROCESS for decarburisation of iron, 7A.
- ROASTING:  
     iron ore in Czechoslovakia, 131A.  
     iron ore in Poland, 131A.
- RÖCHLING STEELWORKS, strip mills, 14A., 141A.
- RÖCKNER ROLLING MILL, 211A.
- ROLLING:  
     billets, cost, 141A.  
     cold, cooling of rolls, 141A.  
     cold, effect on transformer steel, 120A.  
     free-cutting steel, 59A.  
     strip, effect of tension, 15A.  
     temper, strip, 141A.
- ROLLING-MILL PLANT:  
     Algoma Steel Corporation, Ltd., 11A.  
     Atlantic Steel Co., 169A.  
     B.M. Rolling Mills, Ltd., 142A.  
     Carnegie-Illinois Steel Corp., 15A.  
     Dominion Foundries & Steel, Ltd., 137A.  
     Röchling Steelworks, 14A., 141A.  
     Steel Company of Canada, Ltd., 137A.
- ROLLING-MILL PRACTICE, 14A., 59A., 141A., 210A.
- ROLLING-MILL TABLES, torque of rolls, 60A.
- ROLLING MILLS:  
     bearings, synthetic resin, 210A.  
     billet, electric driving, 14A.  
     control instruments for, 16A.  
     electric driving, 14A.  
     electric driving, use of d.c. system, 210A.  
     motors, Ignition rectifiers, 141A.  
     motors, I.R. drop compensation, 210A.  
     plate, electric driving, 14A.  
     Röckner, 211A.  
     roll changing, 15A.  
     strip, 15A., 142A., 211A.  
     strip, Broemel system, 14A., 141A.  
     strip, design, 59A.  
     strip, electric driving, 14A.  
     strip, lubrication, 14A.
- ROLLING PROCESS, theory, 14A.
- ROLLS:  
     changing, 15A.  
     chilled, production, 201A.  
     cooling, 141A.  
     moulding, 10A.
- RUSTON & HORNSBY, LTD., foundry plant, 95A.
- S-CURVES, low alloy steel, 118A.
- ST. PIERRE, examination of nails from, 80A., 154A.

- SALT-BATH CONTAINERS, corrosion, 227A.
- SALT BATHS :  
   use in heat treatment, 17A., 143A., 173A., 212A.  
   use in heat treatment, cyanide determination, 62A.  
   use in heat-treatment, position and shape of electrodes, 107A.  
   use in patenting of wire, 210A.
- SALT-SPRAY TESTS, tests on oxide coatings, 154A.
- SANDBERG PROCESS of treating rails, 221A.
- SCALE, removal from steel, 112A.
- SCALING :  
   cast iron, effect aluminium coatings, 182A.  
   heat-resistant steel, 17A., 63A.  
   steel, effect of vanadium, 17A., 214A.
- SCARFING, billets, 22A., 175A.
- SCRAP :  
   alloy steel, identification by spark tests, 120A.  
   light, use in open-hearth practice, 206A.  
   recovery from slag, 169A., 206A.  
   recovery of tin, 25A.  
   stainless steel, utilisation in America, 12A.
- SEA WATER, corrosion of steel, 191A.
- SECONTE, use in moulding sand, 436P.
- SELENIUM, effect in steel, machinability, 148A.
- SESCO FURNACES :  
   linings, materials for, 63P., 67P.  
   linings, patching process, 66P.  
   production of steel castings, 53 Paper.
- SHARPENING, drills, 212A.
- SHEAR STRENGTH, spot welds, 65A.
- SHEARS, control instruments for, 16A.
- SHEETS :  
   corrosion in soils, 38A.  
   levelling, 59A.  
   stainless steel, properties, 146A.  
   stretch-forming, 140A.  
   thin, drawability, evaluation, 58A.
- SHELL STEEL, manufacture, 11A.
- SHELLS :  
   drawing, 140A.  
   forging, 140A.  
   forging, "one-shot" method, 12A.  
   forging, Witter process, 13A.  
   heat treatment, 107A.  
   moulding, 49A.
- SHETLAND, properties of chromite, 89A.
- SHOTWELD PROCESS for welding stainless steel, 110A.
- SHRINKAGE, malleable cast iron, 48A.
- SIEP-BATH GEAR Co., heat-treatment plant, 173A.
- SILICA :  
   effect on carbon monoxide, decomposition, 3A.  
   effect on iron oxide at high temperatures, 199A.
- SILICA BRICKS. *See* Refractory Materials.
- SILICON :  
   determination in pig iron, 82A.  
   determination in iron and steel, photometric method, 82A.  
   determination, use of photo-electric colorimeter, 205A.  
   effect in cast iron, 31A.  
   effect in cast iron, austenite transformation, 187A.  
   effect in cast iron, carbon saturation, 122A.  
   effect in cast iron, graphitisation, 101A.  
   effect in cast iron, machinability, 148A.  
   effect in free-cutting steel, machinability, 148A.  
   effect in steel, 73A.  
   effect in steel, machinability, 27A.  
   removal from pig iron, 2A.
- SILICON BRIQUETTES, addition to cast iron, 201A.
- SILICON-CARBIDE BRICKS. *See* Refractory Materials.
- SILICON FERRITE, recrystallisation, 223A.
- SILICON IRON :  
   magnetisation near boundaries, 120A.  
   manufacture, 133A.
- SILICON STEEL :  
   effect of cold rolling and annealing, 120A.  
   magnetostriction, 70A.
- SILICON-STEEL CASTINGS, properties, 220A.
- SILICONISED STEEL, wear tests, 147A.
- SILKRAY, use in moulding sand, 436P.
- SILVER, electrodeposition, 113A.
- SINGER PROCESS of phosphatising, 180A.
- SINTER, use in blast-furnaces, 94A., 195A.
- SINTERING :  
   blast-furnace flue dust, 195A.  
   iron ore, 2A., 195A., 206A.  
   iron powders, 95A.  
   manganese ore, 88A.

**SINTERING (contd.)—**

Minette ore, 195*A*.

**SINTERING PLANT :**

heat balances, 89*A*.

Great Lakes Steel Corporation, 195*A*.

Greenawalt, at Julienhütte, 2*A*.

SIOLITE, use in moulding sand, 436*P*.

**SLAG :**

action on refractory materials, 162*A*., 196*A*.

action on silica bricks, 89*A*.

blast-furnace. *See* Blast-Furnace Slag.

control, in open-hearth practice, 204*A*., 206*A*.

recovery of scrap, 169*A*., 206*A*.

vanadium bearing, analysis, 83*A*.

**SLAG-METAL EQUILIBRIA :**

effect of foreign ions, 171*A*.

electric furnace process, 56*A*.

study with use of rotating induction furnace, 104*A*.

SLITTING MILLS, history, 15*A*.

SMELTING, minette ore, 195*A*.

SOCIÉTÉ ANON. DES HAUTS FOURNEAUX, FORGES ET ACIÉRIES DE DENAIN ET D'ANZIN, rimming steel ingots made by, 295 *Paper*.

**SODA ASH :**

use for desulphurisation of cast iron, 98*A*.

use for desulphurisation of pig iron, 133*A*.

SODIUM CARBONATE, use as corrosion inhibitor, 73*P*.

SODIUM CHLORIDE, corrosion of alloys, 125*A*.

SODIUM VANADATE, use as corrosion inhibitor, 73*P*.

**SOILS :**

corrosion of bolts, 126*A*.

corrosion of brass, 127*A*.

corrosion of cast iron, 110*P*.

corrosion of chromium-copper steel, 110*P*.

corrosion of chromium steel, 110*P*., 126*A*.

corrosion of copper and copper alloys, 126*A*., 127*A*.

corrosion of copper-molybdenum steel, 126*A*.

corrosion of copper steel, 110*P*.

corrosion of galvanised steel, 126*A*.

corrosion of ingot iron, 110*P*.

corrosion of iron and steel, 107 *Paper*, 38*A*., 126*A*., 127*A*.

corrosion of lead, 127*A*.

**SOILS (contd.)—**

corrosion of malleable cast iron, 126*A*.

corrosion of pipes, 39*A*.

corrosion of sheets, 39*A*.

corrosion of stainless steel, 127*A*.

corrosion of wrought iron, 110*P*., 126*A*.

corrosion of wrought iron, cadmium plated, 126*A*.

corrosion of zinc, 110*P*., 127*A*.

corrosiveness, determination, 122*P*.

SOLIDIFICATION, steel castings, 203*A*.

**SOLUBILITY :**

hydrogen in iron and iron alloys, 181 *Paper*.

hydrogen in iron-nickel alloys, 181*P*.

hydrogen in nickel steel, 181*P*.

SOUTH AMERICA, mineral resources, 87*A*.

SPARK TESTS, steel, 120*A*.

**SPECIFICATIONS :**

air-cooled blast-furnace slag, British, 167*A*.

aircraft steel, American, 34*A*.

boiler pipes, British, 152*A*.

boiler steel, British, 34*A*.

electric-arc welding plant, British, 146*A*.

gas cylinders, British, 185*A*.

lead-base priming paint, British, 182*A*.

steel for armaments and vehicles, British, 185*A*.

steel, co-ordination, 123*A*.

structural steel for shipbuilding, British, 185*A*.

wire, British, 185*A*.

SPECTROPHOTOMETER, use in analysis, 82*A*.

**SPECTRUM ANALYSIS :**

inclusions, 81*A*.

instruments used in, 152*A*.

determination of copper and tin, 205*A*.

iron and steel, 81*A*.

SPEKKER PHOTO-ELECTRIC ABSORPTIOMETER, use in analysis, 227*A*.

SPINDEL WEAR TEST, effect of testing conditions, 26*A*.

SPINNING, stainless steel, 209*A*.

SPONGE CHROMIUM, production, 131*A*.

**SPRAYING :**

copper, 181*A*.

metals, 115*A*.

phosphate coatings, 180*A*.

SPRING WIRE, properties, 71*A*.



## SPRINGS :

aeronautical instrument, characteristics, 150A.  
 manufacture, 13A.

STAFFORDSHIRE, chain making industry, 106A.

## STAINLESS CLAD STEEL :

production, 113A.  
 production, Jessop method, 113A.

## STAINLESS STEEL :

corrosion in hydrochloric acid, 127A.

corrosion in soils, 127A.

deep drawing and pressing, 209A.

electrodeposition of metals, 180A.

electrolytic cleaning, 112A.

use in aircraft construction, 74A.

use in nitric acid plants, 151A.

welding, 66A., 144A., 145A., 175A.

welding, Shotweld process, 110A.

STAINLESS-STEEL SCRAP, utilisation in America, 12A.

STAINLESS-STEEL SHEETS, properties, 146A.

STAINLESS-STEEL STRIP, annealing furnace, 18A.

STAMPINGS, surface area determination, 176A.

"STASSET" for open-hearth bottoms, 205A.

STATISTICAL ANALYSIS, use in corrosion studies, 156A.

STEAM, reaction with iron, 225A.

## STEEL :

aircraft, specifications, American, 34A.

alloy, analysis, 83A.

alloy, damping capacity, 70A.

alloy, determination of nickel, 82A.

alloy, effect of tin, 141 *Paper*.

alloy (low), properties, 216A.

alloy (low), S-curves, 118A.

alloy (low), use for aircraft construction, 74A., 221A.

alloy (low), weldability tests, 19A.

annealing, bright, 64A.

austenitic, machinability, effect of elements, 148A.

boiler, intercrystalline cracking, 156A.

boiler, specifications, British, 34A.

brittleness, effect of hydrogen, 30A.

bullet-proof, production, 171A.

case-hardened, wear tests, 147A.

case-hardening, selection for gear manufacture, 16A.

clad, production, 113A.

cleaning prior to painting, 23A.

cold-working, pretreatment by phosphatising, 180A.

STEEL (*contd.*)—

corrosion in water, use of inhibitors and their effect on heat transfer, 73 *Paper*.

creep, 149A.

damping capacity, 70A.

dead, 147A.

defects, 119A., 208A.

deoxidation with titanium, 100A.

desulphurisation, 52A.

desulphurisation with calcium silicates, 138A.

desulphurisation in open-hearth process, 170A.

dynamo, effect of cold rolling and annealing, 120A.

effect of boron, 121A.

effect of cold work, 26A.

effect of deoxidisers, 219A.

effect of elements, 117A.

effect of heat treatment, 117A.

effect of hydrogen, 72A.

effect of silicon, 73A.

elastic properties, 119A.

enamel coatings, blisters, 115A.

enamel coatings, effect of oxide coatings, 116A.

evolution of hydrogen, 205P.

fatigue strength at low temperatures, 218A.

flake formation, 53A.

free-cutting, machinability, effect of elements, 148A.

free-cutting, production, 51A., 170A.

free-cutting, rolling, 59A.

fractures, woody, 35A.

grain growth, effect of capillarity in grain boundaries, 36A.

grain size, determination, 124A.

hair-line cracks, effect of carbon, 229P.

hardenability, 69A., 219A.

heat-resistant, properties, 123A.

heat-resistant, scaling, 17A., 63A.

high sulphur, effect of tin, 206A.

high-sulphur, welding flux for, 215A.

high-tensile, weldability tests, 20A., 67A.

high-tensile, welding, 144A., 215A.

killed, addition of aluminium, 206A.

liquid, gas content, 52A.

liquid, gases in, analysis, 80A.

liquid, hydrogen content, 52A.

low-carbon, case-hardening, 143A.

machinability, effect of elements, 27A., 148A.

magnetisation near boundaries, 120A.

STEEL (*contd.*)—

National Emergency, properties, 216A.  
 nitrogen absorption, 206A.  
 non-magnetic, use for wrapping wire, 33A.  
 over-heating, 106A.  
 oxidation, 157P.  
 phosphate coatings, 114A.  
 pickling, 112A., 176A.  
 production, 11A., 50A., 103A., 137A., 169A., 203A.  
 production in resistor furnaces, 11A.  
 quenching, 19A., 117A.  
 recarburisation in open-hearth practice with amorphous graphite, 52A.  
 residual metals, 169A.  
 rimming, Bessemer, manufacture and composition, 295 *Paper*, 327 *Paper*.  
 rimming, carbon diffusion, 357 *Paper*.  
 rimming, open-hearth, carbon content of core, 289P.  
 rimming, open-hearth, composition variation from outside to centre, 345 *Paper*.  
 rimming, open-hearth, manufacture and composition, 283 *Paper*.  
 rimming, open-hearth, sulphides in, 288P.  
 rolling properties, effect of tin, 206A.  
 scale removal, 112A.  
 scaling, effect of vanadium, 17A., 214A.  
 shell, manufacture, 11A.  
 siliconised, wear tests, 147A.  
 specifications, British, 185A.  
 specifications, co-ordination, 123A.  
 sulphite-treated, production, 170A.  
 transformations, effect of diffusion, 77A.  
 transformer, effect of cold rolling and annealing, 120A.  
 use for aircraft construction, 74A.  
 use for moulding of plastics, 172A.  
 weldability tests, 19A., 66A., 109A.  
 welding, spot, 175A.  
 STEEL COMPANY OF CANADA, LTD., plant, 137A.  
 STEEL FOUNDRIES, productive capacity, 202A.  
 STEEL FOUNDRY PRACTICE, British, 98A.  
 STEEL PLANT :  
   Algoma Steel Corporation, Ltd., 11A.

STEEL PLANT (*contd.*)—

Atlantic Steel Co., 169A.  
 Companhia Siderurgica Belgo-Mineira, 11A.  
 Copperweld Steel Co., 203A.  
 Dominion Foundries & Steel, Ltd., 137A.  
 planning of production, 105A.  
 Samuel Fox & Co., Ltd., 203A.  
 Steel Company of Canada, Ltd., 137A.  
 STOKERS, mechanical, for metallurgical furnaces, 43A.  
 STOOLS, for ingot moulds, 56A., 206A., 207A.  
 STRAIN GAUGES, 16A.  
 STRESS :  
   determination, 217A.  
   measurement, use of X-rays, 68A.  
 STRESS-RELIEF, welded joints, 64A.  
 STRESSES :  
   effect on hair-line crack formation, 251P., 253P.  
   in welded joints, 109A.  
   in welded plates, effect of pre-heating, 145A.  
   principal, effect on fatigue strength, 184A.  
   tensile and reversed, structure of metals under, 147A.  
 STRETCH-FORMING, sheets, 140A.  
 STRIP :  
   electrolytic tinning, 24A.  
   levelling, 59A.  
   polishing belts, electric control, 16A.  
   reeling, speed and tension control, 59A.  
   rolling, effect of tension, 15A.  
   stainless steel, annealing furnace, 18A.  
   temper rolling, 141A.  
   width gauge, 16A.  
 STRIP MILLS, 15A., 142A., 211A.  
   Broemel system, 14A., 141A.  
   design, 59A.  
   electric driving, 14A.  
   lubrication, 14A.  
 STRONTIUM ORE, concentration, 89A.  
 STRUCTURAL STEEL :  
   brittleness, effect of elements, 32A.  
   for shipbuilding, specification, British, 185A.  
 STRUCTURE :  
   iron, wüstite and magnetite, 157 *Paper*.  
   metals under tensile and reversed stresses, 147A.  
   nickel cast iron, 223A.  
   nickel steel, 223A.

- SULPHIDES, in rimming steel, 288*P*.  
 SULPHITE-TREATED STEEL, production, 170*A*.  
 SULPHUR :  
   determination in coal and coke, 83*A*.  
   determination in pig iron, 82*A*.  
   determination in steel, 467*P*.  
   determination in steel, limits of accuracy, 468*P*.  
   determination, use of Leco apparatus, 205*A*.  
   effect in cast iron, 151*A*.  
   effect in cast iron, austenite transformation, 187*A*.  
   effect in cast iron, machinability, 148*A*.  
   effect in steel, machinability, 27*A*., 148*A*.  
 SULPHUR DIOXIDE :  
   determination in flue gases, 83*A*.  
   effect in boiler feed water, 189*A*.  
 SULPHUR PRINTS, production, 75*A*.  
 SULPHURIC ACID :  
   corrosion of alloys, 125*A*.  
   corrosion of steel, 191*A*.  
 SURFACE QUALITY, determination, 74*A*.  
 SWELLING, coal, 164*A*., 165*A*.  
 SWELLING TESTS :  
   coal, British Standard method, 164*A*.  
   coal, Gray-King method, 164*A*.  
   coal, Lessing method, 164*A*.  
 SYMBOLS, for heterogeneous equilibria, 153*A*.  
 TACONITE, treatment, 2*A*.  
 TALBOT PROCESS, Witkowitz Works, 103*A*.  
 TANK PARTS, nitriding, 63*A*.  
 TANTALUM ORE DEPOSITS, South America, 87*A*.  
 TARNISHING, metals, 128*A*., 224*A*.  
 TEMPER-BRITTLENESS, structural steel, effect of elements, 32*A*.  
 TEMPER ROLLING, strip, 141*A*.  
 TEMPERATURES :  
   control, in chromium plating, 177*A*.  
   distribution in coke-oven walls, 92*A*.  
   effect of creep strength, 27*A*.  
   high, embrittlement of chromium-molybdenum-nickel steel, 29*A*.  
   high, embrittlement of chromium-molybdenum steel, 29*A*.  
   high, embrittlement of chromium steel, 29*A*., 71*A*.  
 TEMPERATURES (*contd.*)—  
   high, properties of chromium-molybdenum-vanadium steel, 30*A*.  
   high, properties of chromium-nickel steel, 220*A*.  
   low, fatigue strength of steel, 218*A*.  
   measurement, use of Thermocolor pigments, 142*A*.  
 TEMPERING :  
   quenching of steel after, 183*A*.  
   tools, 62*A*.  
 TEMPLETON KENLY Co., heat-treatment plant, 173*A*.  
 TENSILE PROPERTIES, stainless-steel sheets, 146*A*.  
 TENSILE STRENGTH :  
   determined by hardness tests, 218*A*.  
   welded joints, 108*A*.  
 TENSILE TESTS, effect of speed of loading, 25*A*.  
 TESTING MACHINE, corrosion, 224*A*.  
 TESTS :  
   acoustic, 67*A*.  
   agglutinating value, coal, 93*A*.  
   bend, notched-bar, 25*A*.  
   bend, weld metal, 20*A*., 67*A*.  
   bend-fatigue, welded plates, 20*A*.  
   coking, coal, Agde-Damm method, 44*A*.  
   coking, coal, Davis method, 44*A*.  
   coking, coal, Gieseler method, 44*A*., 165*A*.  
   corrosion, atmospheric, 39*A*.  
   creep, boiler tubes, 28*A*.  
   electrical, 68*A*.  
   fillet and plug welds, 145*A*.  
   hardenability, chromium-molybdenum-nickel steel, 148*A*.  
   hardenability, molybdenum steel, 148*A*.  
   hardness, for determining tensile strength, 218*A*.  
   hardness, scatter in, 120*A*.  
   magnetic, 68*A*.  
   moulding sands, 48*A*., 100*A*., 136*A*.  
   non-destructive, 67*A*.  
   permeability, moulding sands, apparatus, 416*P*.  
   pressure, boiler tubes, 28*A*.  
   salt spray, on oxide coatings, 154*A*.  
   spark, steel, 120*A*.  
   swelling, coal, British Standard method, 164*A*.  
   swelling, coal, Gray-King method, 164*A*.  
   swelling, coal, Lessing method, 164*A*.

TESTS (*contd.*)—

- tensile, effect of speed of loading, 25A.
- tool steel, 27A.
- wear, case hardened steel, 147A.
- wear, siliconised steel, 147A.
- weldability, chromium-copper steel, 110A.
- weldability, high-tensile steel, 20A., 67A.
- weldability, steel, 19A., 66A., 109A.

## THERMAL CONDUCTIVITY :

- carbon, 90A.
- fibrous materials, 90A.
- granular material, 90A.
- graphite, 91A.
- insulating bricks, 90A.
- mica, 90A.
- moulding sand, 420P.
- refractory materials, 90A.

## THERMAL EXPANSION, moulding sand, 419P.

## THERMOCOLOR PIGMENTS for measurement of temperatures, 142A.

## THERMOCOUPLES, construction, 60A.

## THERMOMETERS :

- electric-resistance, theory, 60A.
- platinum-resistance, calibration, 60A.

## THICKNESS, gauges for determining, 16A.

## THORIUM, effect in cast iron, 121A.

## TILTING FURNACES :

- brick consumption, 16P.
- linings, 9 *Paper*.

## TIN :

- determination, spectrographic method, 205A.
- effect in alloy steel, 141 *Paper*.
- effect in carbon steel, 141P.
- effect in chromium-molybdenum-nickel steel, 141P.
- effect in chromium-molybdenum steel, 141P.
- effect in chromium-nickel steel, 141P.
- effect in galvanising bath on coatings, 181A.
- effect in high-sulphur steel, 206A.
- effect in manganese-molybdenum steel, 141P.
- effect in nickel steel, 141P.
- effect in steel, rolling properties, 206A.
- electrodeposition, 24A., 113A., 114A., 182A.
- recovery from scrap, 25A.

## TIN ORE DEPOSITS, New Mexico, 1A.

## TINPLATE, production, use of ammonium stannous oxalate baths, 115A.

## TITANIUM :

- deoxidation with steel, 100A.
- determination in alloys, mercury cathode method, 82A.
- effect in cast iron, machinability, 148A.
- effect in chromium-vanadium steel, 31A.
- effect in free-cutting steel, machinability, 148A.

## TITANIUM CARBIDE, in titanium steel, 481P.

## TITANIUM NITRIDE in titanium steel, 481P.

## TITANIUM ORE, concentration, 89A.

## TITANIUM ORE DEPOSITS, South America, 87A.

## TITANIUM OXIDE, effect on iron oxide at high temperatures, 199A.

## TITANIUM STEEL, carbide and nitride particulars, 481P.

## TOOL STEEL :

- heat treatment and selection, 212A.
- ingot moulds for, 56A.
- properties, 144A.
- tests, 27A.
- tungsten, uses, 111A.
- welding, atomic hydrogen, 145A.

## TOOLS :

- cemented carbide, 22A.
- cutting, performance, 22A., 111A.
- tempering, 62A.

## TRACTOR PARTS, forging, 172A.

## TRANSFORMATIONS :

- austenite, in cast iron, effect of elements, 186A.
- austenite in high-speed steel, 76A.
- in nickel steel, 77A.
- in steel, effect of diffusion, 77A.

## TRANSFORMER STEEL, effect of cold rolling and annealing, 120A.

## TROPENAS CONVERTERS, production of steel castings, 135A.

## TUBES :

- boiler, pressure and creep tests, 28A.
- condenser, phosphate coatings, 179A.

## TUNGSTEN ORE DEPOSITS :

- California, 1A.
- Colorado, 1A.
- Idaho, 87A.
- South America, 87A.

## TUNGSTEN STEEL :

- production in Australia, 95A.
- use for magnets, 148A.



**TUNGSTEN TOOL STEEL :**

properties, 144A.

uses, 111A.

**TURBINE BLADES, corrosion, 38A.****TYRES, defects, 69A.****UNDERCOOLING, cast iron, 102A.****UNITED KINGDOM :**

mixer practice, 206A.

specification for air cooled blast-furnace slag, 167A.

specification for boiler pipes, 152A.

specifications for boiler steel, 34A.

specification for electric-arc welding plant, 146A.

specification for gas cylinders, 185A.

specification for lead-base priming paint, 182A.

specifications for steel for armaments and vehicles, 185A.

specification for structural steel for shipbuilding, 185A.

specification for wire, 185A.

steel foundry practice, 98A.

**UNITED STATES :**

blast-furnace practice, 2A.

coal deposits, 1A.

chrome ore deposits, 1A.

chrome ore position, 87A.

consumption of aluminium in steel industry, 53A.

development of duplex process, 137A., 204A.

iron-ore industry, 2A.

manganese ore deposits, 1A., 87A.

manufacture of ferro-chromium, 41A.

mixer practice, 206A.

open-hearth practice, 50A.

refractories for electric furnaces, 90A.

specifications for aircraft steel, 34A.

tin ore deposits, 1A.

tungsten ore deposits, 1A., 87A.

utilisation of stainless steel scrap, 12A.

National Emergency Steels, 216A.

**UPSET FORGING MACHINE, 172A.****VALVES :**

hot blast, design, 198A.

Reiner, for open-hearth furnaces, 11A.

**VANADIUM :**

determination in iron and steel, 83A.

**VANADIUM (contd.)—**

effect in cast iron, machinability, 148A.

effect in free-cutting steel, machinability, 148A.

effect in steel, scaling, 17A., 214A.

recovery from blast-furnace slag, "bottom-reaction" process, 45A.

**VANADIUM-BEARING SLAG, analysis, 83A.****VANADIUM ORE, concentration, 89A.****VANADIUM ORE DEPOSITS, South America, 87A.****VANADIUM STEEL, creep strength, effect of carbon, 149A., 150A.****VILLARI EFFECT, 70A.****WAD ORE, concentration, 195A.****WASTE HEAT BOILERS, 4A.****WATER CIRCULATING SYSTEM :**

microbiological deposits, 189A.

microbiological deposits, bibliography, 189A.

**WATER-LINE ATTACK in corrosion of steel, 73P.****WATERTOWN ARSENAL, centrifugal casting, 49A.****WEAR :**

blast-furnace linings, 162A.

cast iron, 219A.

**WEAR TESTS :**

case hardened steel, 147A.

siliconised steel, 147A.

Spindel, effect of testing conditions, 26A.

**WELD METAL :**

bend tests, 20A., 67A.

hardness, effect of composition, 175A.

**WELDABILITY, copper steel, 150A.****WELDABILITY TESTS :**

chromium-copper steel, 110A.

high-tensile steel, 20A., 67A.

steel, 19A., 66A., 109A.

**WELDED BRIDGES, cracks in, 21A.****WELDED FACINGS, properties, 20A.****WELDED JOINTS :**

corrosion resistance, 215A.

galvanising, 181A.

preheating and stress relieving, 64A.

stresses in, 109A.

tensile strength, 108A.

**WELDED PLATES :**

bend fatigue tests, 20A.

stresses, effect of preheating, 145A.

**WELDING :**

atomic hydrogen, tool steel, 145A.

bronze, cast iron, 175A.

**WELDING (contd.)—**

- chromium - cobalt - molybdenum - nickel steel, 151*A*.
- chromium - columbium - nickel - titanium steel, 151*A*.
- chromium-manganese steel, 151*A*.
- chromium - molybdenum - nickel steel, 151*A*.
- chromium-nickel steel, 151*A*.
- chromium-nickel steel, Shotweld process, 110*A*.
- chromium-silicon-zirconium steel, 144*A*.
- chromium steel, 111*A*.
- electric arc, stainless steel, 66*A*.
- electric arc, transfer of metal, 65*A*.
- high-speed steel tips to carbon steel shanks, 111*A*., 145*A*.
- high-tensile steel, 144*A*., 215*A*.
- pressure vessels, 175*A*.
- spot, mild steel, 175*A*.
- stainless steel, 144*A*., 145*A*., 175*A*.
- WELDING ELECTRODES**, arc, economical use, 174*A*.
- WELDING FLUX**, for high-sulphur steel, 215*A*.
- WELDING MACHINES**, electric, 214*A*.
- WELDING PLANT**, electric arc, specification, British, 146*A*.
- WELDS** :
  - butt, properties, effect of welding procedure, 66*A*.
  - fatigue strength, 146*A*.
  - fatigue strength, effect of notches, 21*A*.
  - fillet, tests, 145*A*.
  - plug, tests, 145*A*.
  - spot, shear and impact strength, 65*A*.
- WERTHEIM EFFECT**, 70*A*.
- WHEELS**, chilled, production, 167*A*.
- WIEDEMAN EFFECT**, 70*A*.
- WIRE** :
  - drawing, backward pull, 106*A*.
  - drawing, formulae for, 13*A*.
  - drawing, heating up of metal, 172*A*.
  - drawing, history, 13*A*.
  - heat-treatment, 62*A*.
  - patenting, use of salt baths, 210*A*.
  - specification, British, 185*A*.
  - spring, properties, 71*A*.

**WIRE (contd.)—**

- wrapping, use of non-magnetic steel, 33*A*.
- WITKOWITZ WORKS**, Talbot process, 103*A*.
- WITTER PROCESS** for forging shells, 13*A*.
- WOOD**, use for drawing dies, 106*A*.
- WROUGHT IRON** :
  - cadmium plated, corrosion in soils, 126*A*.
  - corrosion in soil, 110*P*., 126*A*.
- WÜSTITE**, crystal structure, 157*P*.
- X-RAY DIFFRACTION**, instruments used in, 152*A*.
- X-RAY EXAMINATION** :
  - lattice distortion, 152*A*.
  - metals, 152*A*., 153*A*.
  - use of lead intensifying screens, 221*A*.
- X-RAYS**, use for stress measurement, 68*A*.
- YIELD STRENGTH**, determination, 67*A*.
- ZINC** :
  - corrosion in chloride solutions, 226*A*.
  - corrosion in soil, 110*P*., 127*A*.
  - electrodeposition, 113*A*.
  - molten, effect on malleable cast iron, 181*A*.
  - oxide coatings, 114*A*.
- ZINC COATINGS** :
  - corrosion, 227*A*.
  - electrolytic, corrosion, 190*A*.
  - electrolytic, protective value, 192*A*.
  - replaced by paint coatings, 117*A*.
- ZINC ORE**, concentration, 89*A*.
- ZIRCONIUM** :
  - effect in cast iron, machinability, 148*A*.
  - effect in free-cutting steel, machinability, 148*A*.
  - effect in steel, machinability, 148*A*.
- ZIRCONIUM ORE DEPOSITS**, South America, 87*A*.

## NAME INDEX.

- AAMODT, B. J., acid steel melting, 104A.
- AFANAS'EV, S., free-cutting steel, 51A.
- AITCHISON, C. S., properties of stainless steel sheets, 146A.
- AKIMOV, K., rolling of free-cutting steel, 59A.
- ALLEN, C. J., heat-treated rails, 220A.
- ALLEN, N. P., solubility of hydrogen in iron, 256P.
- ALLEN, W., obituary notice, 492P.
- ALMEN, J. O., stress determination in metals, 217A.
- AMBLER, J. A., elected Associate, 4P.
- AMOS, E., elected Associate, 4P.
- ANDERSON, A. R., tensile tests, 25A.
- ANDERSON, C. T., leaching of man-ganiferous iron ore, 194A.
- ANDREW, J. H., rimming steel, 366P.
- ANDREW, J. H., A. K. BOSE, G. A. GEACH and H. LEE :  
*Paper* : "The Formation of Hair-Line Cracks. Part I," 193P.  
*Joint Discussion*, 244P.  
*Joint Correspondence*, 256P.  
*Authors' Reply*, 270P.
- ANDREW, J. H., A. K. BOSE, H. LEE, and A. G. QUARRELL :  
*Paper* : "The Formation of Hair-Line Cracks. Part II," 203P.  
*Joint Discussion*, 244P.  
*Joint Correspondence*, 256P.  
*Authors' Reply*, 270P.
- ANDREW, J. H., H. LEE, and A. G. QUARRELL :  
*Paper* : "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys," 181P. *Joint Discussion*, 244P. *Joint Correspondence*, 256P. *Authors' Reply*, 270P.
- ANDREWS, W., elected Member, 2P.
- AREND, A. G., bullet-proof steel, 171A.
- AREND, H., wear tests, 26A.
- ARMISTEAD, W. H., determination of iron, 157A.
- ARMSTRONG, E., prevention of rust on steel, 188A.
- ARMSTRONG, G. R., elected Associate, 4P.
- ARNOLD, E. A., electrographic analysis, 157A.
- ARTHUR, J. T., elected Member, 2P.
- ASH, W., rimming steel, 382P.
- ASHCROFT, W., heat-treatment furnaces, 107A.
- ASTON, J. L., elected Associate, 4P.
- ATHEY, J. W., elected Member, 2P.
- ATKIN, chilled rolls, 201A.
- ATTWILL, W. H., water treatment to prevent corrosion, 189A.
- AUER, G., air heaters for blast-furnaces, 133A.
- AULER, E. P., effect of welding procedure on properties of butt-welded stainless steel, 66A.
- AUSEL, W., corrosion of steel, 191A.
- AVERSTEN, J., deseaming of billets, 23A.
- EVERY, H. S., creep of chromium-nickel steel, 220A.
- BABLIK, H. :  
corrosion of galvanised vessels by pig food, 192A.  
corrosion of zinc coatings, 227A.  
galvanising, 181A.
- BACKHAUS, K., individually driven rolls for roll tables, 60A.
- BAGSHAW, B. :  
determination of sulphur and phosphorus in steel, 471P.  
elected Member, 2P.
- BAIER, S., electroplating, 114A., 182A.
- BAILEY, B. L., conversion of magnesite to periclase, 131A.
- BAILEY, C. A., reclamation of lubricating oil, 210A.
- BALDWIN, A. T., galvanising, 24A.
- BALICKI, M., elected Member, 2P.
- BALLARD, J. W., photometric instruments, 152A.
- BANDEL, G. :  
embrittlement of chromium steel, 71A.  
scaling of heat-resistant steel, 17A.  
scaling resistance of alloy steel, 63A.
- BANFIELD, T. A. :  
*Paper* : "Tests on the Corrosion of Buried Ferrous Metals." See HUDSON, J. C.
- BARDENHEUER, P., high-frequency furnaces, 54A., 55A.

- BARDILL, J. D., concentration of manganese ore, 88A.
- BARHEINE, F., paper foundry patterns, 101A.
- BARKER, L. B., contour measurement of wire-drawing dies, 141A.
- BARLOW, T. E., alloying of cast iron, 134A.
- BARNES, W., excavating machines for ore mines, 194A.
- BARRACLOUGH, S.:  
*Paper*: "The Influence of Tin on Alloy Steels." See BOLSOVER, G. R.
- BARRETT, E. P., leaching of manganese carbonate ores, 41A.
- BARRETT, H. N., JUN., magnesite ramming mixtures, 204A.
- BARTLETT, C. W., production of springs, 13A.
- BASSETT, J. B., microscopic examination of metals, 124A.
- BASTOW, J., elected Associate, 4P.
- BAUER, J. T., slag reaction in basic open-hearth practice, 204A.
- BAUKLOH, W.:  
 effect of solids on decomposition of carbon monoxide and methane, 3A.  
 effect of thorium in cast iron, 121A.  
 refining of cast iron in carbon-monoxide/carbon-dioxide mixtures, 7A.
- BAYLEY, W. S., mineral resources of New Jersey, 87A.
- BECK, A. E., recovery of manganese from ore, 88A.
- BECKET, F. M., obituary notice, 493P.
- BEECH, A. S., mechanisation of foundries, 50A.
- BEECHING, R., cavitation erosion of propellers, 37A.
- BEEGHLY, H. F.:  
 determination of nitrogen in steel, 80A.  
 nails from ruins of St. Pierre, 80A., 154A.
- BEHRENDT, G., desulphurisation of pig iron, 94A.
- BEINERT, H., passivity of iron, 190A.
- BELCHER, R., determination of sulphur and phosphorus in steel, 472P.
- BELL, W., JUN., casting of anchors, 202A.
- BENCOWITZ, I., welding flux for high-sulphur steel, 215A.
- BENEDICKS, C.:  
 capillarity in grain boundaries of metals, 36A.  
 corrosion of Ovikak iron, 225A.
- BENSON, L. E., quenching of chromium-nickel steel after tempering, 183A.
- BERGMANN, W. W., ingot-mould stools, 56A., 206A.
- BERK, A. A., intercrystalline cracking of boiler steel, 156A.
- BERLIEN, G. B., heat treatment, 61A.
- BERRIMAN, A. E., effect of contraction and stresses in welds, 109A.
- BESSE, W., use of long-distance gas for firing reheating furnaces, 105A.
- BEVAN, J. I., elected Member, 2P.
- BEVERLEY, L. T., elected Associate, 4P.
- BILL, A. B., malleable iron castings, 49A.
- BINGHAM, J. W., obituary notice, 494P.
- BINNIE, D.:  
*Paper*: "An Ingot of Rimmed Steel Made by the Basic Open-Hearth Process," 283P. *Joint Discussion*, 363P. *Joint Correspondence*, 377P. *Author's Reply*, 384P.
- BIRCH, R. E., blast-furnace refractories, 90A.
- BIRDSALL, G. W., properties of forgings, 26A.
- BISCHOF, F., carbon saturation in cast iron, 122A.
- BISSELL, A. G., weldability tests, 19A., 67A.
- BLACK, L. G., "Hardsteel" drills, 22A.
- BLACKBURN, J., elected Associate, 4P.
- BLAKISTON, J.:  
 moulding sands, 458P.  
 substitution of cast iron for steel castings, 167A.
- BLASCHCZYK, G., isolation of iron carbide, 35A., 222A.
- BLEAKNEY, H. H.,  $Ac_1$  range in nickel steel, 77A.
- BLECKMANN, R., high-frequency furnaces, 55A.
- BLOOM, F. S.:  
 forge furnaces, 139A.  
 reheating furnaces, 105A.
- BLUM, W., lead plating, 24A.
- BOGLE, J. C., hard chromium plating, 24A.
- BOLLENRATH, F., determination of elastic constants, 35A.



- BOLSOVER, G. R., and S. BARRA-CLOUGH :  
*Paper* : "The Influence of Tin on Alloy Steels," 141P.
- BONHOEFFER, K. F. :  
 activation of passive iron in nitric acid, 190A.  
 passivity of iron, 190A.
- BOOT, P. J., core-binders, 459A.
- BOOTE, E. M., obituary notice, 494P.
- BOOTH, H., carbon blocks for blast furnaces, 162A.
- BORSIG, F., corrosion of machine parts, 38A.
- BOSE, A. K. :  
*Paper* : "The Formation of Hair-Line Cracks." See ANDREW, J. H.
- BOSWELL, A., elected Member, 2P.
- BOTTENBERG, W., high-frequency furnaces, 54A.
- BOWMAN, H. T., after-blow in Bessemer practice, 203A.
- BOXALL, D. G., elected Associate, 4P.
- BOYLES, A., undercooling of cast iron, 102A.
- BRADLEY, J. N., linings for Sesci furnaces, 67P.
- BRADSHAW, C. D., elected Member, 2P.
- BRAIDWOOD, W. W., high-duty cast iron, 96A.
- BRAILSFORD, F., magnetostriction in electrical sheets, 70A.
- BRASHARES, C. A., refractories for electric furnaces, 90A.
- BREITLING, K., gasification in small producers, 196A.
- BREMER, E., casting of trench mortar bodies, 100A.
- BREMER, F., phosphate coatings on piston rings, 180A.
- BRICKWEDDE, F. C., platinum resistance thermometers, 60A.
- BRINKMANN, G. :  
 core binders, 10A.  
 short-cycle annealing of malleable cast iron, 98A.
- BROWN, C. E., measurement of atmospheric pollution, 164A.
- BROWN, J. S., fatigue of crankshafts, 184A.
- BROWN, R. H., cathodic protection of metals, 124A.
- BROWN, W. T., by-product coking practice, 44A.
- BRUCHHAUSEN, C., silicon-carbide bricks, 195A.
- BRUCKNER, W. H., weldability of steel, 19A.
- BRYTCZUK, W. L., electrolytic polishing, 186A.
- BUCHANAN, W. Y., tests of moulding sand, 48A.
- BUCHHOLTZ, H. :  
 corrosion cracking of steel, 37A.  
 tests on boiler tubes, 28A.
- BUELL, W. C., JUN., mixer practice, 206A.
- BULAVKIN, A., gas content of liquid steel, 52A.
- BUNGARDT, W., effect of vanadium on scaling of steel, 17A., 214A.
- BURTON, H. H., hydrogen evolution and hair-line crack formation, 244P.
- BUSCH, H., failure of welded bridges, 21A.
- BUTLER, H., obituary notice, 495P.
- CALHOUN, W. A., concentration of manganese-bearing ore, 88A.
- CALLAGHAN, E., tungsten in Idaho, 87A.
- CAMPBELL, G., defects in steel, 208A.
- CAMPBELL, J. D. :  
 electrical instruments for steel industry, 16A.  
 strip mill of Carnegie-Illinois Steel Corp., 15A.
- CAMPBELL, T. C., low-alloy steel for aircraft construction, 221A.
- CAMPBELL, W. E., statistical control in corrosion studies, 156A.
- CASE, R. W., centrifugal casting of guns, 49A.
- CAULFIELD, T. H., elected Member, 2P.
- CENTER, E. J., determination of phosphorus in iron ore, 158A.
- CHARTERIS, W. F., elected Member, 2P.
- CHASE, H. :  
 cold-press work, 13A.  
 forging of tractor parts, 172A.  
 heat treatment of cold-headed products, 18A.  
 phosphate coatings on steel, 114A.  
 plant of Lalanse and Grosjean Mfg. Co., 209A.
- CHESTERS, J. H. :  
 chromite from Shetland, 89A.  
 linings for electric furnaces, 42A.  
 refractories for open-hearth furnaces, 162A.
- CHIPMAN, J., carbon-oxygen equilibrium in liquid iron, 205A.
- CHISWIK, H. H., corrosion-resistance of welds, 215A.

- CHRISTENSEN, A. L., intensifying screens for radiographs, 76*A*.  
 CHUBB, W. F., chilled-iron wheels, 167*A*.  
 CHUYKO, N., sound ingots, 56*A*.  
 CHWORINOFF, N., solidification of castings, 203*A*.  
 CLARK, D., steel castings, 98*A*.  
 CLARKE, L., moulding a marine-engine bed-plate, 49*A*.  
 CLAUSS, J. A., fuel-oil supply system of Great Lakes Steel Corporation, 206*A*.  
 CLAUSSEN, G. E. :  
   fusibility tests for determining weldability, 66*A*.  
   tests of welds, 145*A*.  
 CLEAVES, H. E., high-purity iron, 183*A*.  
 CLEVELAND, C., forging shop of Delaware, Lackawanna and Western Railroad, 58*A*.  
 CLUBLEY, G. H., elected Member, 2*P*.  
 COLBECK, E. W., corrosion of water-circulating systems, 103*P*.  
 COLLACOTT, R. A., corrosion resistance of chromium-nickel steel, 126*A*.  
 COLLINS, A., coke and pig-iron manufacture, 93*A*.  
 COMSTOCK, G. F., effect of deoxidisers on forging steel, 219*A*.  
 CONTRACTOR, G. P., weldability of alloy steel, 109*A*.  
 COOK, E., creep of chromium-nickel steel, 220*A*.  
 COOME, D. E., elected Member, 2*P*.  
 CORNELIUS, H. :  
   effect of composition on properties of welded facings, 20*A*.  
   effect of vanadium on scaling of steel, 17*A*., 214*A*.  
   ferrous materials used in aircraft, 74*A*.  
 COWLIN, F. J., properties of steel at high temperatures, 149*A*.  
 COYNE, T. D., fatigue of welds at low temperatures, 218*A*.  
 CRAFTS, W., carbides in low-chromium steel, 222*A*.  
 CRAIG, J. W., basic linings for open-hearth furnaces, 42*A*.  
 CROWTHER, J., elected Member, 2*P*.  
 CURRIE, E. M., cast iron crankshafts, 134*A*.  
 CURTIS, F. W., induction hardening of tools, 212*A*.  
 CURTIS, J. A., colorimetric analysis, 82*A*.  
 DAASCH, H. L., notch sensitivity of welds, 21*A*.  
 DANIELS, F. C. T., elected Member, 2*P*.  
 DANNÖHL, W. :  
   iron-aluminium-nickel alloys, 78*A*., 224*A*.  
   iron-aluminium-nickel diagram, 77*A*.  
 DARRAH, W. A., ferro-alloy production in Brazil, 199*A*.  
 DARTON, N. H., anthracite in Pennsylvania, 1*A*.  
 DATTISMAN, E. J., JUN., co-operation between open-hearth and rolling-mill departments, 206*A*.  
 DAVEY, H. J., obituary notice, 495*P*.  
 DAVIES, E., coke and pig-iron manufacture, 93*A*.  
 DAVIES, L., elected Member, 2*P*.  
 DAVIS, H. W., substitutes for cobalt, 185*A*.  
 DAVIS, J. D. :  
   coking tests of coal, 44*A*.  
   swelling of coal, 165*A*.  
 DAVISON, D. W., titanium carbides and nitrides, 482*P*.  
 DAWSON, W. J., moulding sands, 455*P*.  
 DEAN, R. S., recovery of manganese from ores, 88*A*.  
 DEARDEN, J., properties of welded joints, 108*A*.  
 DE FOREST, A. V. :  
   precision springs, 71*A*.  
   tensile tests, 25*A*.  
 DEHLINGER, U., intermetallic phases, 153*A*.  
 DE KEYSER, W., elected Member, 2*P*.  
 DE LANGE, S. G. P., suitability of mild steel for arc welding, 110*A*.  
 DELMONTE, J., steel moulds for plastics, 172*A*.  
 DE LORENZI, O., firing of boilers with blast-furnace gas and coke breeze, 163*A*.  
 DENISON, I. A., corrosion of metals in soils, 127*A*.  
 DESCH, C. H., rimming steel, 369*P*.  
 DESCHAMPS, J. L. G., obituary notice, 496*P*.  
 DESMOND, J., graphite crucibles, 74*A*.  
 DESMOND, J. K., steels for plastic moulds, 122*A*.  
 DEVANEY, F. D., concentration of manganese ore, 88*A*.  
 DICHGANS, H., costs and prices in iron industry, 47*A*.

- DICKENS, P., recovery of iodine and potassium chloride from flue dust, 199A.
- DICKIE, H. A., rimming steel, 366P.
- DIEPSCHLAG, E. :  
centrifugal casting, 10A.  
cupola practice, 47A.
- DINSDALE, C., repair of coke ovens, 5A.
- DISSTON, H. C., steels for plastic moulds, 122A.
- DITTMAR, H., hydraulic plants for Bessemer works, 57A.
- DOANE, F. B., Magnafix method of detecting cracks, 68A.
- DODD, F. G., elected Member, 2P.
- DONALDSON, J. W. :  
carbon steels, 216A.  
non-destructive tests of metals, 67A.
- DORR, J. V. N., tungsten in California, 1A.
- DRECHSLER, W., hardening of steel, 214A.
- DROSSBACH, P., arc furnaces, 138A.
- DRUMM, J. H., JUN., steel plant in Brazil, 11A.
- DRYUPIN, A., blowing-out of blast-furnaces, 45A.
- DUCKWITZ, C. A., tests on boiler tubes, 28A.
- DUFFEK, V., phosphate coatings, 179A.
- DUFFY, N. F. :  
refractory materials for arc furnaces, 43A.  
slag/metal equilibrium in arc furnaces, 56A.
- DURRANS, J., elected Member, 2P.
- DURRANS, P. H., elected Member, 3P.
- DURYEE, L. M., drying moulding sand with infra-red lamps, 101A.
- DWYER, P. :  
casting plough parts and pipe fittings, 134A.  
core blowers, 101A.  
moulding of iron castings, 202A.  
plant of American Naval-Yard foundry, 135A.
- DYER, R. C., porosity in castings, 49A.
- DYER, W. E. S., boiler plant of Algoma Steel Corporation, 3A.
- EADY, M., foundry practice, 95A.
- EASH, J. T. :  
effect of ladle additions on cast iron, 101A.
- EASH, J. T. (*contd.*)—  
moisture control and preheating of cupola blast, 97A.  
structure of nickel steel and nickel cast iron, 223A.
- EBERLE, F., copper-bearing steel, 150A.
- EDSALL, H. L., salt-bath hardening furnaces, 107A.
- EDSON, A., hardness of weld metal, 175A.
- EDWARDS, J. D., oxide coatings, 114A.
- EICHHOLZ, W., desulphurisation of pig iron, 94A.
- EICHINGER, A., temperature rise in wire drawing, 173A.
- EILENDER, W., corrosion of steel, 191A.
- EISENSTECKEN, F., potential changes of iron-zinc couples, 38A.
- ELCOCK, E. W., elected Member, 3P.
- ELLABY, C. H., protective coatings, 182A.
- ELLINGER, G. A. :  
weldability tests, 67A.  
weldability tests of steel, 19A.
- ELLIS, O. W., forgeability of metals, 140A.
- ELLIS, R. P. P., elected Associate, 4P.
- ELVEY, L. E., sharpening of drill steel, 212A.
- EMDE, G., moulding sands, 9A.
- EMERICK, H. B., duplex process, 137A., 204A.
- ENDELL, J., clay substance in moulding sand, 100A.
- ENDELL, K., clay substance in moulding sand, 100A.
- ENGEL, A. L. :  
grinding of carnotite ore, 194A.  
ore-dressing, 88A.
- ENGELBERT, U., refining of cast iron in carbon-monoxide/carbon-dioxide mixtures, 7A.
- ENZIAN, G. H., nails from ruins of St. Pierre, 80A., 154A.
- ESCHER, K., wear of cast iron, 219A.
- ESS, T. J. :  
plant of Atlantic Steel Co., 169A.  
plant of Copperweld Steel Co., 203A.  
plant of Dominion Foundries and Steel, Ltd., 137A.  
plant of Steel Company of Canada, Ltd., 137A.
- ESSER, H. :  
effect of temperature on creep strength, 27A.  
wear tests, 26A.
- EVANS, E. C., fuel economy in iron industry, 91A.

- EVANS, G. S. :  
 desulphurisation of cast iron, 98A.  
 desulphurisation of pig iron, 133A.
- EVANS, N. L., elected Member, 3P.
- EVANS, R. L., leaching of manganese carbonate ores, 41A.
- EVANS, U. R. :  
*Paper* : "A Study of Some Soluble Inhibitors, with Special Reference to Heat Transfer with Water-Line Attack." See THORNHILL, R. S.  
 corrosion of iron and zinc in chloride solutions, 226A.  
 hair-line crack formation, 257P.  
 oxidation reactions, 175P.
- EVERETT, L. E., defects in castings, 101A.
- EYRE, A. W., elected Associate, 4P.
- FABER, H., phosphatising before cold-work, 180A.
- FARABEE, R. L., elected Member, 3P.
- FARLOW, V. R., induction hardening, 174A.
- FASTOVSKIY, B., Bessemer steel, 220A.
- FAUST, G. T., magnesia-silica system, 196A.
- FEIGENBAUM, S., duplex process, 137A., 204A.
- FELLOWS, J. A., creep of chromium-nickel-steel, 220A.
- FERON, H., elected Member, 3P.
- FINE, M. M. :  
 concentration of manganese-bearing ore, 131A., 194A.  
 concentration of manganese ore, 88A.  
 concentration of manganiferous iron ore, 88A.  
 concentration of wad ore, 195A.
- FISHER, H. C., rammed linings for electric furnaces, 43A.
- FISHER, R. B. :  
 concentration of manganese-bearing ore, 131A.  
 concentration of wad ore, 195A.
- FITTERER, G. R., gases in acid open-hearth steel, 206A.
- FLETCHER, T., patching of Sesci furnace linings, 66P.
- FOLKNER, M. H., Nicarb process of case-hardening, 63A.
- FORSBERG, H. J. U., obituary notice, 496P.
- FOSTER, B., elected Member, 3P.
- FOUNTAIN, L. L., electric driving of rolling mills, 210A.
- FOX, A. L., recovery of manganese from ores, 88A.
- FOXWELL, G. E., carbon deposition in coke-oven roofs, 197A.
- FRICKE, R. :  
 equilibrium between iron, iron oxide, hydrogen and water, 225A.  
 lattice distortion, 152A.
- FRIES, C., JUN., tin in New Mexico, 1A.
- FRY, Miss E. B., elected Member, 3P.
- FUCHS, W., coking pressures, 164A.
- FULLER, E., sintering plant of Great Lakes Steel Corporation, 195A.
- FULTON, J. S., effect of coke rate on gas composition in blast furnaces, 45A.
- FUSCO, A. J., cadmium plating, 113A.
- GALL, D. C., elected Member, 3P.
- GALL, J., gasification in small producers, 196A.
- GARRETT, G. B., obituary notice, 497P.
- GARZULY-JANKE, R., corrosion of galvanised vessels by pig food, 192A.
- GASE, D. C., elected Member, 3P.
- GEACH, G. A. :  
*Paper* : "The Formation of Hair-Line Cracks." See ANDREW, J. H.
- GEBAUER, K., chromium coatings, 177A.
- GEHM, H. W., utilisation of waste pickling liquor, 112A.
- GELLER, W. :  
 corrosion of steel, 191A.  
 resistor furnaces for steel making, 11A.
- GIMMY, A., degree of saturation in cast iron, 215A.
- GINSBERG, S. I., leaching of manganese carbonate ores, 41A.
- GLASS, D. K., obituary notice, 498P.
- GNIDA, E., use of coke-oven gas in open-hearth furnaces, 207A.
- GODDARD, E. N., manganese in Montana, 1A.
- GOLD, J. D., use of blown metal in basic open-hearth practice, 206A.
- GOLDEN, J. J., pig-ore process, 205A.
- GOL'DMAN, V., manufacture of chromium-nickel steel from scrap, 54A.



- GOLDSCHMIDT, H. J. :  
*Paper* : "The Crystal Structures of Fe, FeO and  $\text{Fe}_3\text{O}_4$  and their interrelations," 157P. *Correspondence*, 175P. *Author's Reply*, 177P.
- GOODISON, W. S., obituary notice, 498P.
- GOODMAN, W., determination of copper and nickel in steel, 158A.
- GÖRISSEN, J., desulphurisation of iron, 52A.
- Goss, J. H., permanent magnets, 148A.
- GOTTA, A., resistance of chromium-nickel steel to nitric acid, 192A.
- GÖTZL, F., galvanising, 181A.
- GRAHAM, A. K., salt spray tests of oxide coatings, 154A.
- GRAPER, L. G., sulphite-treated steel, 170A.
- GRAY, A. G., lead plating, 24A.
- GRDINA, YU., flame hardening of rails, 62A.
- GREAVES, E. I., elected Associate, 4P.
- GREEN, A. T., carbon blocks for blast-furnaces, 162A.
- GREEN, J. R., Brown system of fuel control, 206A.
- GREENAWALT, J. E., open-hearth sinter, 206A.
- GREGG, A. W. :  
 production of steel castings, 135A.  
 side-blown converters, 99A.
- GREGG, J. L., accelerated atmospheric corrosion test, 39A.
- GREGORY, E. :  
 hydrogen solubility and hair-line crack formation, 248P.  
 limits of accuracy in sulphur determinations, 469P.
- GRIFFEN, J., cleaning of coal, 5A.
- GRIFFITHS, E., thermal conductivity of materials, 90A.
- GRIMSHAW, L. C., heat treatment of molybdenum high-speed steel, 16A.
- GROSSMANN, M. A., hardenability of steel, 219A.
- GROSVENOR, A. W.,  $\text{Ac}_1$  range in nickel steel, 77A.
- GROVE, H. A., stainless steel scrap, 12A.
- GRUCA, E. P., impact strength of spot welds, 65A.
- GRÜN, R., blast-furnace slag cement, 46A., 199A.
- GRÜTZMACHER, F. E., elimination of dust and noise in foundries, 136A.
- GUDGEON, W., moulding of iron castings, 203A.
- GULBRANSEN, E. A., oxide films on iron, 127A.
- GURRY, R. W., solubility of carbon in gamma iron, 186A.
- GUTHMANN, K. :  
 ore-preparation plants, 89A.  
 pigments for temperature measurement, 142A.  
 preparation of iron ore, 131A.
- GUTHRIE, R. G., nitriding tank parts, 63A.
- HAASE, L. W., effect of biological processes on corrosion, 188A.
- HALL, F. W., elected Associate, 4P.
- HALL, G., core sand mixtures, 10A.
- HALL, N., surface area of stampings, 176A.
- HALL, W. H., elected Associate, 4P.
- HALLS, E. E. :  
 analytical control of nickel-plating solutions, 228A.  
 thickness measurement of nickel coatings, 177A.
- HALVORSON, O. A., corrosion of bolts, 126A.
- HAMER, P., corrosion of water-circulating systems, 103P.
- HAMILTON, O. H., oxidation and tarnishing of metals, 224A.
- HAMMOND, A. F., production of cast-iron cylinder cover, 168A.
- HAMNETT, G. J., elected Member, 3P.
- HAMPTON, G. T., elected Member, 3P.
- HANEMANN, H., signs for heterogeneous equilibria, 153A.
- HANLEY, H. R., electrolytic cleaning of metals, 112A.
- HARBORD, F. W., obituary notice, 489P.
- HARKER, D., surface replicas for use with electron microscope, 221A.
- HARRINGTON, L. C., drying of lignite, 197A.
- HARRIS, P., elected Associate, 4P.
- HARTLEY, A., elected Associate, 4P.
- HARTLEY, A. L., flame hardening, 213A.
- HASNER, L., corrosion tests by potential measurements, 224A.
- HATFIELD, W. H. :  
 alloy steels, 73A.  
 damping capacity of engineering materials, 70A.  
 hair-line crack formation, 249P.

- HATFIELD, W. H. (*contd.*)—  
 limits of accuracy in sulphur determinations, 468*P.*  
 rimming steel, 363*P.*, 374*P.*  
 standard methods of analysis, 476*P.*
- HAUTTMANN, H., notched-bar bend tests, 25*A.*
- HAYDEN, H., planning and technical department for foundry, 47*A.*
- HAYWOOD, C., elected Member, 3*P.*
- HAZLETT, T. H., stretch forming of sheets, 140*A.*
- HEEREN, M. H., corrosion testing machine, 224*A.*
- HEINRICH, H., effect of phosphorus in cast steel, 122*A.*
- HELLBRÜGGE, J., effect of solids on decomposition of carbon monoxide and methane, 3*A.*
- HEMMING, F. J., obituary notice, 498*P.*
- HENGEMÜHLE, W., scatter in hardness tests, 120*A.*
- HENRY, O. H., fatigue of welds at low-temperatures, 218*A.*
- HERASYMENKO, P., slag-metal equilibria, 171*A.*
- HERRES, S. A., control of cupola blast, 200*A.*
- HERRINGTON, C. F., pulverised coal, 132*A.*
- HERTY, C. H., JUN., use of soft ore in open-hearth practice, 206*A.*
- HERZIG, A. J., hardenability of steel, 69*A.*
- HESELGRAVE, J. L., elected Associate, 4*P.*
- HESS, F. O., radiant-cup burners for heat-treatment furnaces, 61*A.*
- HESS, W. F., spot welding of high-tensile steel, 144*A.*, 215*A.*
- HEUMANN, T., iron/iron-sulphide/-calcium-sulphide system, 36*A.*
- HEWETT, D. F., manganese in Arkansas, 87*A.*
- HEYES, J. :  
 spectrum analysis of inclusions, 81*A.*  
 surface quality of materials, 74*A.*
- HEYN, H. M., heat treatment of wire, 62*A.*
- HICKMAN, M. J., thermal conductivity of materials, 90*A.*
- HICKSON, E. F., paint coatings, 117*A.*
- HIEGEL, J. M., high-purity iron, 183*A.*
- HINDSON, R. D., tin in high-sulphur steel, 206*A.*
- HINMAN, C. W. :  
 drawing and forming dies, 106*A.*  
 redrawing of shells, 140*A.*
- HOAR, T. P., hydrogen in steel, 266*P.*
- HODGSON, G. H., elected Member, 3*P.*
- HOGGE, H. J., platinum resistance thermometers, 60*A.*
- HÖGEL, H., phosphatising, 179*A.*
- HOLDEN, A. H., protective atmospheres in hardening furnaces, 107*A.*
- HOLDEN, H. A. :  
*Paper* : "Tests on the Corrosion of Buried Ferrous Metals." See HUDSON, J. C.
- HOLLAND, E., feeding of malleable iron castings, 48*A.*
- HOLLINDERBÄUMER, W., converter practice for steel castings, 9*A.*
- HOLM, V. C. F., elimination of oxide films on heating in vacuum, 213*A.*
- HOLMES, C. R., properties of coke, 198*A.*
- HOLT, G. J., mining of Minnesota iron ore, 194*A.*
- HOLTMANN, W., properties of alloy steel, 149*A.*
- HONEYMAN, A. J. K., hair-line crack formation, 261*P.*
- HÖNIG, H., resistor furnaces for steel making, 11*A.*
- HOOK, C. R., efficiency in steelworks production, 204*A.*
- HOSKING, N., steel foundry practice, 98*A.*
- HOTOP, W., magnets from sintered iron-nickel-aluminium alloys, 46*A.*
- HOUDREMENT, E. :  
 isolation of iron carbide, 35*A.*, 222*A.*  
 tensile properties of steels annealed in hydrogen, 30*A.*
- HOWARD, E. J. L., properties of cast iron, 31*A.*
- HOWARD, H. C., density and porosity of carbonaceous materials, 93*A.*
- HOWARD, J. M., elected Member, 3*P.*
- HOWARD, W., elected Member, 3*P.*
- HOWAT, D. D., electrostatic precipitation of gases, 5*A.*
- HOWDEN, P., elected Member, 3*P.*
- HOWIE, T. W., chromite from Shetland, 89*A.*
- HOWLAND, A. L., chromite in Montana, 1*A.*
- HOWSON, H. O., hair-line crack formation, 264*P.*
- HOYT, S. L., stainless clad steel, 113*A.*
- HUDDLE, A. U., hair-line crack formation, 262*P.*

- HUDSON, J. C., T. A. BANFIELD and H. A. HOLDEN :  
*Paper* : "Tests on the Corrosion of Buried Ferrous Metals," 107P. *Correspondence*, 127P. *Authors' Reply*, 129P.
- HUGILL, W., product of reaction between silica brick and slag, 89A.
- HUME-ROTHERY, W., G. V. RAYNOR and A. T. LITTLE :  
*Paper* : "On the Carbide and Nitride Particles in Titanium Steels." *Further Discussion*, 481P. *Authors' Reply*, 486P.
- HUNTER, M. A., reducing nickel content of nickel-steel castings, 33A.
- HURST, H. M., elected Associate, 4P.
- HURST, T. L., slagging of refractories, 162A.
- HUTSON, A. E., pyrometry, 60A.
- HUTTL, J. B., manganese in Montana, 1A.
- HYSLOP, J. F., slagging of refractories, 196A.
- IMHOFF, W. G., galvanising, 114A.
- IPSEN, C. L., electric heat-treatment furnaces, 18A., 61A.
- ISENBURGER, H. R., lead screens for X-rays, 221A.
- JACKSON, A. :  
*Paper* : "The Linings of Large Basic Open-Hearth Tilting Furnaces," 9P. *Correspondence*, 16P. *Authors' Reply*, 19P.
- JAENICHEN, E., patenting of wire in salt baths, 210A.
- JAY, A. H., chromite from Shetland, 89A.
- JELLINGHAUS, W., manganese steel for magnets, 27A., 149A.
- JENKINS, C. G., elected Associate, 4P.
- JENKINS, I., bright annealing of steel, 64A.
- JENNINGS, C. J., electric welding machines, 214A.
- JOHANSEN, F. C., detection of flaws in axles, 183A.
- JOHNS, R. L., elected Associate, 4P.
- JOHNSON, H. W., effect of coke properties on blast-furnace practice, 7A.
- JOHNSON, P. H., tinplating, 115A.
- JOHNSON, R. A. C., elected Member, 3P.
- JOHNSTON, T. L., concentration of manganese-bearing ore, 88A., 131A., 194A.
- JONES, D. G., elected Associate, 4P.
- JONES, E., elected Associate, 4P.
- JONES, J. H. :  
 coking coals of Durham, 4A.  
 national emergency steel, 216A.
- JONES, V. W. :  
 briquetting of soft ore, 206A.  
 removal of enamel from scrap, 206A.
- JOSEPH, T. L. :  
 concentration and smelting of iron ores in United States, 2A.  
 desulphurisation of iron in open-hearth process, 170A.  
 effect of manganese on desulphurising power of calcium silicates, 138A.  
 rotating induction furnace, 104A.
- JOY, J. D., elected Member, 3P.
- JURETZKE, H., alloy steel castings, 220A.
- KAIN, C. H. :  
 production of steel castings, 135A.  
 synthetic moulding sand, 462P.
- KAISER, H. F., intensifying screens for radiographs, 76A.
- KALISCHER, P. R., powder metallurgy, 8A.
- KASSEM, M. A., reduction of iron ore with hydrogen, 200A.
- KATSEN, L., gas content of liquid steel, 52A.
- KATZEN, L. G., gases evolved from liquid steel, 80A.
- KAUFFELD, G. H., lubrication systems for strip mills, 14A.
- KAYSER, J. A., refractories for malleable-iron furnaces, 90A.
- KAYSER, J. F., magnetic powder method of crack detection, 218A.
- KEELEY, L. F., ingot moulds for tool steel, 56A.
- KEIL, F., utilisation of blast-furnace slag, 94A.
- KELLEY, F. C., powder metallurgy, 46A.
- KELLS, R. P., heat treatment of molybdenum high-speed steel, 16A.
- KEMMER, F. R., ferro-alloy manufacture in Australia, 95A.
- KEMPF, H., analysis of pig iron, 82A.

- KEMSLEY, C. G., alloy steels for rock drills, 73*A*.
- KENTS, G., slitting mills, 15*A*.
- KENYON, A. F., electric driving of rolling mills, 14*A*.
- KERLE, W. L., rimming steel, 377*P*.
- KESSNER, H., effect of nitrogen in chromium-nickel steel, 121*A*.
- KIESSLER, H., effect of elements on the temper brittleness and hot brittleness of structural steel, 32*A*.
- KING, C. D., use of scrap and pig iron in open-hearth process, 169*A*.
- KING, J., moulding of cast iron cylinder cover, 168*A*.
- KINNAIRD, D. W., case hardening of steel, 143*A*.
- KIRCHBERG, H., microstructure of iron ore, 76*A*.
- KITCHING, E. G., elected Associate, 4*P*.
- KLINGER, P. :  
determination of alloy additions in steel, 83*A*.  
isolation of iron carbide, 35*A*, 222*A*.
- KNIPP, E., moulding sands, 9*A*.
- KOCH, W., determination of alloy additions in steel, 83*A*.
- KOEBEL, N. K., controlled atmospheres, 211*A*.
- KOOTZ, T., nitrogen absorption by iron alloys, 30*A*.
- KOPAJA, L., cost analysis in steel works, 11*A*.
- KOPP, H. :  
cupola practice, 200*A*.  
phosphatising before cold-work, 180*A*.
- KORPIUN, J., corrosion resistance of electrogalvanised coatings, 192*A*.
- KOSHIK, A., manufacture of chromium-nickel steel from scrap, 54*A*.
- KOSTER, J., substitutes for cobalt, 185*A*.
- KOTH, A., drying of lignite, 197*A*.
- KRÄCHTER, H. :  
basic Bessemer process, 103*A*.  
control of basic Bessemer process, 204*A*.
- KRANER, H. M., wear of blast-furnace linings, 162*A*.
- KRATH, E., determination of alloy additions in steel, 83*A*.
- KRAUSE, H., coating of stainless steel, 180*A*.
- KRAUSE, R., phosphatising, 178*A*.
- KREIM, J., case-hardening of chromium-manganese steel, 19*A*.
- KRICHEL, M., production of micrographs of cast iron, 124*A*.
- KRISCH, A., properties of steel, 26*A*.
- KROENIG, W. O., pickling of steel, 176*A*.
- KRÜGER, L., foamed blast-furnace slag, 7*A*.
- KRYNITSKY, A. I., elastic properties of alloy cast iron, 31*A*.
- KUDICKE, K., cost analysis in steel works, 11*A*.
- KULP, R. K., woody fracture in steel, 35*A*.
- LAIDLER, G., elimination of vibrations in drop-hammers, 57*A*.
- LAMB, F. D. :  
concentration of flue dust, 166*A*.  
concentration of manganese nodules, 88*A*.
- LAND, G. W., determination of fusain in coal, 158*A*.
- LANDAU, R., corrosion of binary alloys, 125*A*.
- LARDGE, H. E., butt-welding of high-speed steel tips to mild steel, 145*A*.
- LARICHEV, W., chromium-molybdenum-vanadium steel, 30*A*.
- LARSON, L. J., metal transfer in arc welding, 65*A*.
- LASKY, S. G., manganese in New Mexico, 1*A*.
- LAWRENCE, H., weldability of steel, 109*A*, 66*A*.
- LECKIE, A. H., dust catchers for gas producers, 6*A*.
- LEDING, M. J., ignition rectifiers for motors, 141*A*.
- LEE, H. :  
*Paper* : "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys." See ANDREW, J. H.  
*Paper* : "The Formation of Hair-Line Cracks." See ANDREW, J. H.  
rimming steel, 383*P*.
- LEHMANN, H., clay substance in moulding sand, 100*A*.
- LEMM, H. P., wide strip mills, 59*A*, 211*A*.
- LEMMON, D. M. :  
tungsten in California, 1*A*.  
tungsten in Idaho, 87*A*.



- LEMON, F. A., and H. O'NEILL :  
*Paper*: "The Production in Rotary Furnaces of Steel for Castings," 53P. *Appendix A*. A Patching Process for Sesci Furnace Linings. By T. FLETCHER, 66P. *Appendix B*. Tests on Refractory Lining Materials. By J. N. BRADLEY, 67P. *Correspondence*, 71P. *Authors' Reply*, 72P.
- LENDL, A. E., rolling mill practice, 141A.
- LENZ, G. P., JUN., testing terms and methods, 67A.
- LETENDRE, G., elected Member, 3P.
- LEUTWILER, R. W., JUN., effect of pre-heating temperature on shrinkage stresses in welded plates, 145A.
- LEWIS, K. B., history of wire drawing, 13A.
- LIBSCH, J., iron powders, 95A.
- LICHY, C. M., production of shell steel, 11A.
- LIFSHITS, S., defects in steel, 53A.
- LINDEMUTH, L. B., open-hearth practice in Australia, 206A.
- LINDSAY, R. I., elected Associate, 4P.
- LINDSAY, R. W., graphitisation of cast iron, 102A.
- LINFORD, A., pyrometry, 60A.
- LINLEY, A., substitute high-speed steels, 73A.
- LISTON, R., elected Associate, 4P.
- LLOYD, G. C., obituary notice, 499P.
- LOACH, G. O., cupola practice, 8A.
- LOCKE, F. A., controlled atmospheres, 61A.
- LÖFQUIST, H., corrosion of Ovifak iron, 225A.
- LOGAN, K. H., soil corrosion, 38A., 126A.
- LOHRER, W., equilibrium between iron, iron oxide, hydrogen and water, 225A.
- LOIB, F., embrittlement of chromium steel at high temperatures, 29A.
- LONGDEN, E., cupola charges, 134A.
- LONGNECKER, C., plant of Algoma Steel Corp., 11A.
- LONGWELL, J. R.:  
 carbide dies for drawing special shapes, 13A.  
 carbide drawing dies, 141A.
- LORD, W. M., core binders, 461P.
- LORIG, C. H.:  
 control of cupola blast, 200A.  
 effect of hydrogen in malleablising process, 167A.  
 undercooling of cast iron, 102A.
- LOSCHILOV, S., Bessemer steel, 220A.
- LOUGHREY, D. R., Bessemer converter plant, 169A.
- LOUX, J. H., Witter shell-forging process, 13A.
- LOVERING, T. S., tungsten in Colorado, 1A.
- LUCKIE, J. B., water cooling of open-hearth furnaces, 104A.
- LUEG, W.:  
 backward pull in wire drawing, 106A.  
 effect of tension during cold-rolling of strip, 15A.  
 surface quality of materials, 74A.  
 temperature rise in wire drawing, 173A.
- LUMPKIN, L. B., temperature control in chromium plating, 177A.
- LUSTMAN, B., film formation on metals, 79A.
- LYNAM, T. R., chromite from Shetland, 89A.
- MCADAM, D. J., JUN.:  
 effect of stresses on fatigue, 184A.  
 elastic properties of metals, 119A.  
 technical cohesive strength of metals, 119A.  
 technical cohesive strength and yield strength of metals, 216A.
- MCCAFFERY, P., X-ray examination of castings, 153A.
- MCCARTHY, R. H., hot-quenching of high-speed steel, 76A.
- MCCARTNEY, J. T., swelling of coal, 165A.
- MACCONOCHIE, A. F.:  
 abrasive disc cutting, 112A.  
 effect of hot and cold work on steel, 26A.  
 flow of metal in forging, 13A.  
 forge furnaces, 105A., 139A.  
 forging of crankshafts, 13A.  
 forging practice, 140A.  
 induction heating, 107A.  
 production of bushes and gears from powdered iron, 46A.  
 resistance heating of forgings, 209A.  
 upset-forging, 173A.
- McDONALD, J. H., use of Chrom-X in steelmaking, 56A.
- McELWEE, R. G., alloying of cast iron, 134A.

- MACGREGOR, C. W., tensile tests, 25A.
- MACHU, W. :  
copper coatings, 181A.  
effect of electric current on acid attack on iron, 226A.  
phosphatising, 177A.  
pickling of steel in presence of inhibitors, 23A.
- McKIMM, P. J. :  
open-hearth practice, 52A., 207A.  
open-hearth process, 103A.
- MACKINNEY, J. J., Shotweld process of welding stainless steel, 110A.
- McLAREN, A. W., elected Member, 3P
- McLEAN, H. M., elected Member, 3P.
- McLOUGHLIN, T. J., organisation of fuel department, 163A.
- MACNAIR, P. M., rimming steel, 370P.
- McNEIL, I., elected Associate, 4P.
- McQUAID, H. W., properties of carbon and low-alloy steels, 117A.
- MAGES, M., Magnafux method of detecting cracks, 68A.
- MAGRATH, J. G., flame hardening, 143A.
- MAIER, C. G., sponge chromium, 131A.
- MAILÄNDER, R., weldability of high-tensile steel, 20A.
- MANTEL, W., effect of silicon in structural steel, 73A.
- MANTERFIELD, D., determination of sulphur and phosphorus in steel, 474P.
- MARIN, J., creep of metals, 149A.
- MARQUAND, H. S., welding of stainless steel, 110A., 145A.
- MARTIN, G., stress measurement by X-rays, 68A.
- MARTINDALE, R. G., magnetostriction in electrical sheets, 70A.
- MASARI, S. C., graphitisation of cast iron, 102A.
- MASON, B. H., awarded Carnegie Research Grant, 2P.
- MASON, H., cleaning of castings, 136A.
- MATHERS, F. C., tinplating, 115A.
- MATHIEU, K., transformation curves in cases of restricted diffusion, 77A.
- MATIS, H. A., impact strength of spot-welds, 65A.
- MATHEWS, S., elected Member, 3P.
- MAURER, E., effect of elements on temper brittleness and hot-brittleness of structural steel, 32A.
- MAWHINNEY, M. H. :  
quenching of steel, 19A.  
reheating furnaces, 209A.
- MEBS, R. W., elastic properties of metals, 119A.
- MEHL, F., recrystallisation of silicon ferrite, 223A.
- MEHL, R. F., decomposition of austenite, 223A.
- MEIERLING, H., effect of thorium in cast iron, 121A.
- MERCHANT, H. J., awarded Carnegie Research Grant, 2P.
- MERRITT, H. E., elected Member, 3P.
- METCALFE, N., macrographic examination of metals, 34A.
- METHLEY, B. W., limits of accuracy in sulphur determinations, 468P.
- MEYER, E. R., induction hardening, 174A.
- MIDDEL, W., recovery of iodine and potassium chloride from flue dust, 199A.
- MIKA, T. F., drawability of thin metals, 58A.
- MILEY, H. A., oxidation and tarnishing of metals, 128A., 224A.
- MILLER, E. K., dry-air blast, 166A.
- MILLER, V., sintering of manganese ore, 88A.
- MILLS, D. M., specifications for steel, 123A.
- MILNES, A. H., drop-forging aircraft parts, 58A.
- MINKOFF, I., elected Associate, 4P.
- MISER, H. D., manganese in Arkansas, 87A.
- MITCHELL, J. :  
*Paper* : "Comparative Study of Three Ingots Received from Soc. Anon. des Hauts Fourneaux, Forges et Aciéries de Denain et d'Anzin, at Denain, France," 295P. *Joint Discussion*, 363P. *Joint Correspondence*, 377P. *Author's Reply*, 386P.
- Paper* : "Rimming Steel. Report on Four Ingots of Basic Bessemer Steel," 327P. *Joint Discussion*, 363P. *Joint Correspondence*, 377P. *Author's Reply*, 386P.
- MITCHELL, R. W., cleaning of metals, 175A.
- MOHLER, F., electric driving of rolling mills, 14A.
- MÖLLER, H. :  
determination of elastic constants, 35A.  
microstructure of iron ore, 76A.  
stress measurement by X-rays, 68A

- MONTGOMERY, T. B., temper mills, 141A.
- MOONEY, R. H., clay slurry additions to moulding sand, 136A.
- MOORE, C. J., elected Member, 3P.
- MORRIS, D. O., machinability of metals, 27A.
- MORRIS, J. S., training of open-hearth operators, 204A.
- MORROGH, H. :  
defects in cast iron, 75A.  
detection of alloy elements in cast iron, 75A.  
metallography, 74A.
- MORSE, L. G. E., elected Member, 3P.
- MORTON, B. B., corrosion of metals in refinery plant, 189A.
- MOSS, F. C., obituary notice, 500P.
- MOTT, R. A., caking and swelling of coal, 164A.
- MOULDING MATERIALS SUB-COMMITTEE, Second Report, 393P.
- MUELLER, J., forging practice, 105A.
- MUIR, W. P., forging shells, 12A.
- MÜLLER, F., corrosion tests by potential measurements, 224A.
- MUMFORD, A. R., use of blast-furnace gas under boilers, 197A.
- MUNROE, J. M., handling of castings, 202A.
- MURFITT, G., determination of sulphur in steel, 471P.
- MURRAH, E. S., strip reeling, 59A.
- MURRAY, S., electrodeposition of metals, 113A.
- NAESER, G. :  
basic Bessemer process, 103A., 204A.  
recovery of vanadium from iron, 45A.
- NAGLER, C., effect of elements on austenite transformation in cast iron, 186A.
- NEERFELD, H. :  
determination of elastic constants, 35A.  
transformation curves in cases of restricted diffusion, 77A.
- NEILSON, J. H. S., elected Associate, 4P.
- NEUMAN, D., mathematics for wire mills, 13A.
- NEUMANN, G., entropy, 4A.
- NEWBRANDER, S. M., use of blown metal in basic open-hearth practice, 206A.
- NEWELL, W. C. :  
hair-line crack formation, 254P.  
determination of sulphur and phosphorus in steel, 473P.  
remarks on paper by Hume-Rothery and others, 483P.  
rimming steel, 371P.
- NICHOLAS, I. A., bottoms for basic open-hearth furnaces, 205A.
- NIEZOLDI, O., ancient cast iron, 95A.
- NORBURY, A. L., remarks on Goldschmidt's paper, 177P.
- NORBURY, C., moulding of crusher shell, 101A.
- NORRIS, G. L., obituary notice, 501P.
- OATES, J. A., elected Member, 3P.
- O'CONNELL, W. J., JUN., microbiological deposits in water, 189A.
- ODE, W. H., agglutinating value of coal, 93A.
- OFFENHAUER, C. M., carbides in low-chromium steel, 222A.
- OLDACH, S., corrosion of binary alloys, 125A.
- OLDERSHAW, F., effect of sulphur and manganese in cast iron, 151A.
- OLIVER, D. A., hair-line crack formation, 245P.
- ONDERDONK, P. T., stress relieving of welds, 64A.
- O'NEILL, H. :  
*Paper* : "The Production in Rotary Furnaces of Steel for Castings."  
*See* LEMON, F. A.  
defects in rails and tyres, 69A.  
rimming steel, 382P.
- OPITZ, H., wear of cast iron, 219A.
- OSHRY, H. I., photometric instruments, 152A.
- OSSWALD, E., determination of elastic constants, 35A.
- OVERATH, W., phosphatising, 180A.
- PACKHAM, P. C., elected Associate, 4P.
- PAGE, T. H. D., electrolytic corrosion of buried metals, 126A.
- PALMER, T. J., bronze-welding of cast iron, 175A.
- PAQUET, J., sintering of Minette ore and flue dust, 195A.
- PARKE, R. M., hardenability of steel, 69A.
- PARKER, C. M., national emergency steels, 216A.
- PARKER, T. W. and J. F. RYDER :  
*Paper* : "Investigations on 'Falling' Blast-Furnace Slags," 21P.

- PARKES, W. B., elected Member, 3*P*.  
 PARKIN, G. :  
   determination of sulphur in steel, 476*P*.  
   hair-line crack formation, 267*P*.  
   titanium carbides and nitrides, 485*P*.  
 PARKS, B. C., determination of fusain in coal, 158*A*.  
 PARRY, V. F., drying of lignite, 197*A*.  
 PATEK, P. :  
   design of forging dies, 172*A*.  
   forging dies, 140*A*.  
 PATEMAN, L. W., elected Associate, 4*P*.  
 PATERSON, D. G. P., training of metallurgists, 124*A*., 221*A*.  
 PATTERMANN, O., hardening cracks in high-speed steel, 108*A*.  
 PAVLIS, F., effect of acetic acid on metals, 226*A*.  
 PEARSON, J. M., measurement of corrosion, 127*A*.  
 PECK, C. E., controlled atmospheres, 173*A*.  
 PEILE, J. B., elected Member, 3*P*.  
 PEMBERTON, H. N., tests of welds, 146*A*.  
 PEOPLES, J. W., chromite in Montana, 1*A*.  
 PETER, W., precipitation hardening and creep strength of columbium steel, 72*A*.  
 PETERMANN, F. B., sintering of manganese ore, 88*A*.  
 PETERSEN, C., effect of stresses on structure of metals, 147*A*.  
 PETERSON, R. G., sintering of manganese ore, 88*A*.  
 PETERSON, W., stress relieving of welds, 64*A*.  
 PETZOLD, F., analysis of vanadium-bearing slag, 83*A*.  
 PFANNENSCHMIDT, C. W., cast iron cylinder liners, 122*A*.  
 PHILBROOK, W. O. :  
   use of Leco apparatus in analysis, 205*A*.  
   use of photometer in analysis, 205*A*.  
 PIGOTT, E. C., analysis of ferrous metals, 80*A*.  
 PIKE, J. A., sintering of manganese ore, 88*A*.  
 PILLING, N. B., structure of nickel steel and nickel cast iron, 223*A*.  
 PINDER, H. W. :  
   hair-line crack formation, 259*P*.  
   high-speed steel, 207*A*.  
   elected Member, 3*P*.  
 PITROVSKIY, G., blowing-out of blast-furnaces, 45*A*.  
 POLA, W., cupola practice, 96*A*.  
 POMP, A., effect of cold-rolling and annealing on Watt losses of dynamo and transformer steel, 120*A*.  
 POWELL, R. W., thermal conductivity of materials, 90*A*.  
 POWIS, G., mechanical stokers for metallurgical furnaces, 43*A*.  
 PRAY, H., accelerated atmospheric corrosion test, 39*A*.  
 PUMPHREY, W. I., elected Associate, 4*P*.  
 PUSCH, R., corrosion cracking of steel, 37*A*.  
 PYATT, W. F., elected Member, 3*P*.  
 QUARRELL, A. G. :  
   *Paper* : "The Determination of the Solubility of Hydrogen in Iron and Iron Alloys." *See* ANDREW, J. H.  
   *Paper* : "The Formation of Hair-Line Cracks." *See* ANDREW, J. H.  
   rimming steel, 368*P*.  
 RALSTON, R. R., magnesia-silica system, 196*A*.  
 RAMBERG, W., properties of stainless steel sheets, 146*A*.  
 RAMMLER, E., gasification in small producers, 196*A*.  
 RAMP, P. R., casting of hollow rolls, 10*A*.  
 RAMSEY, E. L., sulphite-treated steels, 170*A*.  
 RAYMOND, L. E., hardening of steel in salt baths, 212*A*.  
 READ, E. B., slagging of refractories, 162*A*.  
 READER, L. J., leaching of manganese carbonate ores, 41*A*.  
 REAGAN, W. J. :  
   contamination of steel by alloy elements, 169*A*.  
   steel-making practice, 50*A*.  
 REES, O. W. :  
   determination of ash in coal, 158*A*.  
   determination of fusain in coal, 158*A*.  
 REESE, D. J. :  
   cupola practice, 47*A*., 96*A*., 167*A*.  
   increase of production in foundries, 99*A*.



- REICHERT, J. W., Japanese iron industry, 46A.
- REICHSFELD, W. M., elected Member, 3P.
- REIMER, G., cold rolling, 141A.
- REIN, A., hot-blast mains and valves, 198A.
- REINARTZ, P. M., American steel expansion programme, 206A.
- REITMEISTER, W., moulding sands, 9A.
- RENWICK, W., steel moulds for plastics, 172A.
- REPLOGLE, H. E., air-hardening steels for forging dies, 172A.
- RESOW, H., production capacity of steel foundries, 202A.
- REULECKE, W., failure of welded bridges, 21A.
- REYNOLDS, D. A., properties of coke, 198A.
- RICHARD, K., embrittlement of alloy steel at high temperatures, 29A.
- RICHARDSON, K., elected Associate, 4P.
- RICKER, R., planning production in ironworks, 105A.
- RIDSDALE, N. D., moulding sands, 455P.
- RIEDRICH, G. :  
effect of nitrogen in chromium-nickel steel, 121A.  
embrittlement of chromium steel at high temperatures, 29A.  
heat-resistant steel, 123A.
- RIENDEAU, J. D., elected Associate, 4P.
- RIGBY, G. R., carbon blocks for blast-furnaces, 162A.
- RITTER, E., recovery of vanadium from iron, 45A.
- ROBERTSON, F. W., levelling machine for sheets, 59A.
- ROBIETTE, A. G., heat treatment, 106A.
- ROBINSON, A., rimming steel, 365P.
- ROCKEFELLER, H. E., cutting of billets, 66A.
- ROCKEFELLER, J. W., JUN., aircraft instrument springs, 150A.
- ROCKWELL, M. M., stretch forming of sheets, 140A.
- ROESNER, G., phosphatising, 178A.
- ROGERS, B., elected Member, 3P.
- ROGNER, H., cleaning of metals, 176A.
- ROHRMAN, F. A., effect of acetic acid on metals, 226A.
- ROLL, F. :  
corrosion of cast iron, 225A.
- ROLL, F. (*contd.*)—  
corrosion of salt bath containers, 227A.  
effect of aluminium coatings on cast iron, 182A.  
effect of molten zinc on malleable cast iron, 181A.
- ROONEY, T. E., limits of accuracy in sulphur determinations, 469P.
- ROSENSTIEHL, F. E., lubricating oils, 210A.
- ROSS, D., obituary notice, 501P.
- ROTHERS, H., potential changes of iron-zinc couples, 38A.
- ROTHERHAM, L., damping capacity of engineering materials, 70A.
- ROTTER, A., open-hearth process at Witkowitz, 103A.
- RÜBMANN, H., planing of blooms, 23A.
- RUDORFF, D. W. :  
effect of molybdenum and titanium in chromium-vanadium steel, 31A.  
effect of vanadium and molybdenum on creep strength of steel, 150A.  
hardening cracks in high-speed steel, 108A.  
hydrogen in steel and cast iron, 72A.  
solidification of castings, 203A.
- RUECKEL, W. C., heating of coke ovens, 92A.
- RUSSELL, G. A. V., steel manufacture, 51A.
- RUSSELL, T. F., hair-line crack formation, 251P., 265P.
- RUTENBECK, T., cavitation corrosion of metals, 155A.
- RYDER, F. :  
costs in open-hearth practice, 51A.  
fuel costs for reheating furnaces, 43A., 91A.
- RYDER, J. F. :  
*Paper* : "Investigations on 'Falling' Blast-Furnace Slags."  
*See* PARKER, T. W.
- SACCHI, V. P., protective value of phosphate and oxide coatings, 192A.
- SACHS, G., properties of forgings, 118A.
- SAEGER, C. M., JUN., elastic properties of alloy cast iron, 31A.
- SAGE, A. M., elected Associate, 4P.
- ST. CLAIR, L. J., performance of cutting tools, 22A.

- SAMPLE, J. A., spectrographic analysis in steelworks, 205A.
- SAMUELS, M. L., effect of hydrogen in malleablising process, 167A.
- SAND, H. J. S., polarographic analysis, 228A.
- SANDBERG, G. H., welding of stainless steel pressure vessels, 175A.
- SANDERS, L. W., production of steel castings, 135A.
- SANDERS, T. H., obituary notice, 501P.
- SANDHOFF, A. G., coking pressures, 164A.
- SANDS, G. A., properties of stainless steel, 151A.
- SANDSTEDE, K., determination of sulphur dioxide in flue gases, 83A.
- SARETZKY, E. M., pickling of steel, 176A.
- SARJANT, R. J., hair-line crack formation, 246P.
- SCHACK, C. H. :  
beneficiation of manganese ore, 194A.  
concentration of manganese ore, 41A.
- SCHAEFER, V. J., surface replicas for use with electron microscope, 221A.
- SCHÄFER, R., hardening of steel, 214A.
- SCHAFMEISTER, P., electrolytic polishing of metals, 34A.
- SCHERER, R., effect of nitrogen in chromium-nickel steel, 121A.
- SCHIKORR, G., atmospheric corrosion of iron, 187A.
- SCHLAIN, D., electrodeposition of manganese, 194A.
- SCHLESINGER, G., machinability of steel, 111A.
- SCHLIEMANN, O., spectrum analysis, 81A.
- SCHLÖTTER, M., corrosion of electrolytic zinc coatings, 190A.
- SCHMAHL, N. G. :  
behaviour of iron oxides with other oxides, 198A.  
relation between oxygen pressure, temperature, and composition in  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  system, 166A.
- SCHMELLENMEIER, H., corrosion of electrolytic zinc coatings, 190A.
- SCHMITZ, H., effect of temperature on creep strength, 27A.
- SCHNEIDER, C. E., obituary notice, 491P.
- SCHOFIELD, F. H., elected Member, 3P.
- SCHOFIELD, T. H., elected Member, 3P.
- SCHÖNWÄLDER, F. H., reversing valves for open-hearth furnaces, 11A.
- SCHRADER, H. :  
elimination of dust and noise in foundries, 137A.  
tensile properties of steel annealed in hydrogen, 30A.
- SCHRENK, H. H. :  
measurement of atmospheric pollution, 164A.  
photometric instruments, 152A.
- SCHRODER, C. R., spot welding of high-tensile steel, 144A., 215A.
- SCHROEDER, W. C., intercrystalline cracking of boiler steel, 156A.
- SCHRUPP, C., Greenawalt sintering plant, 2A.
- SCHUBERT, H. :  
*Paper* : "The First Cast-Iron Cannon Made in England," 131P.
- SCHULTE, F., heat-resistant steel, 123A.
- SCHULTZE, F., effect of tension during cold-rolling of strip, 15A.
- SCHUSTER, L., phosphatising, 178A., 180A.
- SCHWARZ, M. VON, cavitation of metals, 155A.
- SCHWARZ, W. :  
determination of silicon, 82A.  
spectrum analysis of inclusions, 81A.
- SCHWIEDESEN, H. :  
pin distribution on converter bottoms, 50A., 203A.  
thermal efficiency of furnaces, 4A.
- SCOTT, F. W. :  
desulphurisation of iron in open-hearth process, 170A.  
effect of manganese on desulphurising power of calcium silicates, 138A.  
rotating induction furnace, 104A.
- SEFING, F. G., production of castings, 201A.
- SEIL, G. E., chrome ores, 42A.
- SELVIG, W. A. :  
agglutinating value of coal, 93A.  
determination of ash in coal, 158A.
- SHARPE, D., elected Member, 3P.
- SHELTON, S. M. :  
concentration of flue dust, 166A.  
concentration of manganese-bearing ore, 131A., 194A.  
concentration of manganese nodules, 88A.

- SHELTON, S. M. (*contd.*)—  
 concentration of manganese ore, 88A.  
 concentration of manganiferous iron ore, 88A.  
 concentration of wad ore, 195A.  
 grinding of carnotite ore, 194A.  
 ore dressing, 88A.
- SHERMAN, W. F., low-alloy steel for aircraft construction, 221A.
- SHORT, M. N., microscopic determination of ore minerals, 34A.
- SHUBINA, N., flame hardening of rails, 62A.
- SHULER, G., cementing high-speed steel tips to carbon steel shanks, 111A.
- SHUTE, D. H., elected Associate, 5P.
- SIDDLE, W., elected Member, 3P.
- SIEBEL, E., theory of rolling, 14A.
- SILVERMAN, L., determination of copper and nickel in steel, 158A.
- SILVERTHORN, R. W., colorimetric analysis, 82A.
- SIMS, C. E. :  
 addition of aluminium to killed steel, 205A.  
 defects in enamel coatings, 116A.
- SKEATES, F. B., side-blown converters, 99A.
- SKERL, J. G. A., core sand, 460P.
- SLATER, L. E., moulding of cast iron cylinder cover, 168A.
- SMALLEY, O., brake drums, 134A.
- SMITH, A. E. McRAE, high-duty cast iron, 48A.
- SMITH, D. W., elected Member, 3P.
- SMITH, E. W. P., arc welding of stainless steel, 66A.
- SMITH, G. V., JUN., decomposition of austenite, 223A.
- SMITH, R. C., JUN., density and porosity of carbonaceous materials, 93A.
- SMITH, R. E., moisture control and preheating of cupola blast, 97A.
- SMITH, R. P., obituary notice, 502P.
- SMITH, S., flame hardening, 213A.
- SMITH, T. B. :  
 accuracy in analysis, 474P.  
 by-product recovery, 5A.
- SONNTAG, J., phosphate coatings, 179A.
- SPEAKMAN, C. H., atomic hydrogen welding of tool steel, 145A.
- SPENCER, G. T., elected Member, 3P.
- SPRARAGEN, W. :  
 corrosion-resistance of welds, 215A.  
 fusibility tests for determining weldability, 66A.  
 tests of welds, 145A.
- SPRAY, S., elected Member, 3P.
- SQUIRE, C. E., obituary notice, 503P.
- STACKELBERG, M. VON, determination of alloy additions in steel, 83A.
- STAMP, E., elected Associate, 5P.
- STANDARD METHODS OF ANALYSIS SUB-COMMITTEE :  
*First Report. Further Discussion*, 467P. *Sub-Committee's Reply*, 479P.
- STANFELD, G. :  
 damping capacity of engineering materials, 70A.  
 obituary notice, 503P.
- STANLEY, J. K., recrystallisation of silicon ferrite, 223A.
- STAPPENBECK, R., mineral deposits in South America, 87A.
- STECK, R., planning production in ironworks, 105A.
- STEEL CASTINGS RESEARCH COMMITTEE :  
 Second Report of the Moulding Materials Sub-Committee, 393P. *Discussion*, 455P. *Correspondence*, 461P. *Sub-Committee's Reply*, 463P.
- STEFFES, M., sintering of Minette ore and flue dust, 195A.
- STEINER, J., laboratory arc furnaces, 151A.
- STEINMETZ, M. H., determination of elements in alloys, 82A.
- STEPHENS, H. A., tests of moulding sand, 100A.
- STEVEN, W., elected Associate, 5P.
- STEVENSON, W. W. :  
*Paper* : "A Note on Diffusion in Rimming Steel on Soaking at About 1300° C." See SWINDEN, T.
- STEWART, I. :  
 case-hardening of gears, 62A.  
 dry-cyaniding, 63A.  
 gas carburising, 107A., 143A.  
 gear-tooth failures, 147A.  
 nitriding of high speed steel, 63A.  
 steels for case-hardening, 16A.
- STEWART, R. C., salt baths for case-hardening, 143A.
- STIELER, C., cupola practice, 47A.
- STOLTZ, G. E., speed control of rolling-mill motors, 210A.
- STONE, M. D., electro-tinning, 24A.

- STONES, J. M., moulding of crusher shell, 101A.
- STRAUSS, J., chrome ore requirements of United States, 41A.
- SULLIVAN, J. D., refractory materials, 3A.
- SURAU, F., gating of castings, 49A.
- SWAIN, S. M., fireclay brick, 3A.
- SWINDEN, R., elected Associate, 5P.
- SWINDEN, T. :  
*Paper* : "Rimming Steel. Additional Studies of the Composition Variation from Outside to Centre," 345P. *Joint Discussion*, 363P. *Joint Correspondence*, 377P. *Author's Reply*, 388P.  
 hair-line crack formation, 259P.  
 rimming steel, 376P., 380P.
- SWINDEN, T., and W. W. STEVENSON :  
*Paper* : "A Note on Diffusion in Rimming Steel on Soaking at About 1300° C.," 357P. *Joint Discussion*, 363P. *Joint Correspondence*, 377P. *Authors' Reply*, 388P.
- SZUBINSKI, W., weldability of high-tensile steel, 20A.
- TAFFS, H. J., photographs of metals, 34A.
- TAMARIN, M. D., temperature distribution in coke-oven walls, 92A.
- TARASOV, L. P., classification of scrap by spark testing, 120A.
- TARASOV, P. P., nails from ruins of St. Pierre, 154A.
- TAYLOR, D. :  
 defects in steel, 119A.  
 tool steels, 212A.  
 elected Member, 3P.
- TAYLOR, J. R., strip mill of Carnegie-Illinois Steel Corp., 15A.
- TAYLOR, N. W., refractory materials, 162A.
- TAYLOR, W. J., hardness tests for estimating tensile strength, 218A.
- TEDDS, D. F. B., elected Associate, 5P.
- TEMPLETON, R. B., cast iron crankshafts, 134A.
- THACKWELL, F. E., beneficiation of manganese ore, 194A.
- THANHEISER, G. :  
 analysis by drop reactions, 157A.  
 polarographic determination of vanadium and chromium, 83A.  
 spectrum analysis, 81A.
- THAYER, T. P., chromite in Oregon, 1A.
- THOMAS, B. :  
 "dead" steel, 147A.  
 heat treatment of die blocks, 65A.  
 heat treatment and work-effect on steel, 106A.  
 nitrided cast iron, 173A.  
 tool steel, 27A.
- THOMAS, L. A., elected Associate, 5P.
- THOMSON, J., defects in steel, 208A.
- THÖNNESSEN, F., cleaning of blast-furnace gas, 6A.
- THORNHILL, R. S. :  
*Paper* : "A Study of Some Soluble Inhibitors, with Special Reference to Heat Transfer with Water-Line Attack," 73P. *Part I.*—Explanatory Statement and Résumé of Conclusions. By U. R. EVANS, 74P. *Part II.*—Description of the Research. By R. S. THORNHILL, 83P. *Correspondence*, 103P. *Authors' Reply*, 104P.
- THORNTON, B. M., determination of dew point of gases, 132A.
- THRING, M. W., use of low-grade fuel in producers, 165A.
- THUM, A. :  
 effect of stresses on structure of metals, 147A.  
 embrittlement of alloy steel at high temperatures, 29A.
- TICE, E. A., flame-cleaning of structural steel, 23A.
- TIMBRELL, J., moulding of gear wheels, 168A.
- TIMMERMANN, D. :  
 changing of rolls, 15A.  
 strip mills, 14A., 141A., 211A.
- TINDULA, R. W., iron ore for basic open-hearth process, 204A.
- TINKER, G. P., arc furnaces, 104A.
- TINSLEY, D., elected Associate, 5P.
- TIPPER, A., corebinders, 202A.
- TISDALE, N. F., effect of boron in steel and cast iron, 121A.
- TITUS, A. C., analysis of steel, 157A.
- TIVERTON, THE RT. HON. THE VISCOUNT, elected Member, 3P.
- TOBIAS, P. :  
 core binders, 10A.  
 short cycle annealing of malleable cast iron, 98A.
- TOFAUTE, W., embrittlement of chromium steel, 71A.
- TOMKINS, S. S., determination of sulphur in coal and coke, 83A.



- TOOTLE, C. R., elected Associate, 5P.  
 TOWN, H. C., presses for sheet metals, 58A.  
 TOY, F. L., plasticity of chrome ore, 205A.  
 TOY, T. L., use of photometer in analysis, 205A.  
 TRAVERS, H. A., electric driving of rolling mills, 210A.  
 TROST, A., X-ray examination, 152A.  
 TUCKER, R. C., moulding sands, 457P.  
 TUCKER, W. M., heavy nickel plating, 24A.  
 TUCKERMAN, L. B., properties of stainless steel sheets, 146A.  
 TURNER, H. R., steel cartridge cases, 58A.  
  
 UHLING, H. H., effect of hydrochloric acid on stainless steel, 127A.  
 UHLITZSCH, H., Maurer's diagram for cast iron, 67A.  
 ULLMAN, F. E., recovery and preparation of scrap, 169A.  
 UNGER, A. M., impact strength of spot welds, 65A.  
 UNGERSBÖCK, O. :  
     effect of electric current on acid attack on iron, 226A.  
     pickling of steel in presence of inhibitors, 23A.  
 UTTON, D., elected Member, 4P.  
  
 VAN DER HOEVEN, B. J. C., effect of coking rate on by-products, 197A.  
 VASHENKO, K. I., iron-silicon-carbon alloys, 133A.  
 VASILEV, V. E., iron-silicon-carbon alloys, 133A.  
 VATCHAGANDHY, J. S., weldability of alloy steel, 109A.  
 VAUGHAN, E. J. :  
     determination of sulphur in steel, 478P.  
     use of Spekker absorptiometer in analysis, 227A.  
 VAUGHN, F. F., induction hardening, 174A.  
 VDOVENKOV, M., blowing out of blast-furnaces, 45A.  
 VINCENT, J. D., concentration of manganese ore, 41A.  
 VIPOND, J. S., sulphur prints, 75A.  
 VOGEL, R., iron/iron-sulphide/calcium-sulphide system, 36A.  
 VOGT, F. W., bearings for rolling mills, 210A.  
  
 VOLK, K. E. :  
     electrolytic polishing of metals, 34A.  
     scaling resistance of alloy steel, 63A.  
 VOLTERRA, R., iron powders, 95A.  
 VRATSKIY, M., recrystallisation of boiler plate, 68A.  
  
 WADDINGTON, E. S., suitability of mild steel for arc welding, 110A.  
 WAGNER, E., clay substance in moulding sand, 100A.  
 WAITE, G. C., elected Member, 4P.  
 WAKELIN, J. H., JUN., magnetisation near boundaries, 120A.  
 WALKER, A. W., elected Associate, 5P.  
 WALKER, G. W., deep etching, 75A.  
 WALKER, S., tests of moulding sand, 136A.  
 WALKER, T. R., elected Member, 4P.  
 WALL, T. F. :  
     arc furnaces, 207A.  
     high frequency furnaces, 12A.  
 WALLACE, E. M., effect of hydrochloric acid on steel, 127A.  
 WALLFRED, C. L., leaching of manganese-carbonate ores, 41A.  
 WALTER, D., determination of copper and nickel in steel, 158A.  
 WALTER, K., equilibrium between iron, iron oxide, hydrogen and water, 225A.  
 WALZEL, R., definition of terms "Bruch" and "Riss," 119A.  
 WASHBURN, T. S., hot metal charges for basic open-hearth furnaces, 205A.  
 WATERKAMP, MARIA, analysis by drop reactions, 157A.  
 WEAN, R. J., strip mills, 142A.  
 WEBSTER, R., cleaning of castings, 10A.  
 WEHRICH, R. :  
     determination of silicon, 82A.  
     non-magnetic wrapping wire, 33A.  
     spectrum analysis of inclusions, 81A.  
 WEIKEL, R. A., instrument department in steelworks, 137A.  
 WERNER, O., bend tests of weld metal, 20A.  
 WESLEY, W., coatings for condenser tubes, 179A.  
 WESLY, W., corrosion of boilers due to feedwater, 189A.  
 WEST, J. H., strickle moulding, 101A.  
 WEST, J. L. :  
     determination of phosphorus in steel, 472P.

- WEST, J. L. (*contd.*)—  
 limits of accuracy in sulphur determinations, 469*P*.  
 elected Member, 4*P*.
- WEST, W., elected Member, 4*P*.
- WEVER, F., precipitation hardening and creep strength of columbium steel, 72*A*.
- WHITCHER, J., corrosion of cast iron in soil, 127*P*.
- WHITCOMB, A. J., charging of blast-furnaces, 198*A*.
- WHITE, A. B., electric welding machines, 214*A*.
- WHITELEY, J. H., rimming steel, 371*P*.
- WHITLOCK, T. M., elected Member, 4*P*.
- WHITTEMORE, H. L., properties of stainless-steel sheets, 146*A*.
- WIEDERHOLT, W., phosphate coatings, 179*A*.
- WIESTER, H. J., weldability of high-tensile steel, 20*A*.
- WILCOCK, R., elected Member, 4*P*.
- WILLARD, H. H., determination of phosphorus in iron ore, 158*A*.
- WILLEMS, J., polarographic determination of vanadium and chromium, 83*A*.
- WILLIAMS, A. E., elected Associate, 5*P*.
- WILLIAMS, C. G., fatigue of crankshafts, 184*A*.
- WILLIAMS, C. H., patching of rotary furnace linings, 71*P*.
- WILLIAMS, L. H., elected Associate, 5*P*.
- WILLIAMS, M. L.:  
 weldability tests, 67*A*.  
 weldability tests of steel, 19*A*.
- WILLIAMS, R. E. H., linings for tilting furnaces, 18*P*.
- WILLIAMS, S. R., elected Associate, 5*P*.
- WILLIAMS, S. V., bright annealing of steel, 64*A*.
- WILLIAMS, T. H., detection of nickel in alloy steel, 82*A*.
- WILLIAMS, W. D., magnetostriction phenomena, 70*A*.
- WILLIS, K., elected Associate, 5*P*.
- WILMS, O. H., effect of elements on the temper brittleness and hot brittleness of structural steel, 32*A*.
- WILSON, J. F., slag-line attack on tilting furnace linings, 16*P*.
- WILSON, W., elected Member, 4*P*.
- WINLACK, G. D., descaling of billets, 175*A*.
- WINLOCK, J., Shotweld process of welding stainless steel, 110*A*.
- WOLDMAN, N. E., cadmium plating, 113*A*.
- WOLFE, G. F., bridges for handling iron ore, 2*A*.
- WOLFF, L., scarfing of billets, 22*A*.
- WOOD, C. E., leaching of manganese-carbonate ores, 41*A*.
- WOOD, F. C., dry-air blast, 7*A*.
- WOOD, W. P., effect of elements on austenite transformation in gamma iron, 186*A*.
- WOOLAS, P., elected Member, 4*P*.
- WOOLMAN, J.:  
 hair-line crack formation, 253*P*.  
 titanium carbides and nitrides, 484*P*.
- WRIGHT, J. H., elected Member, 4*P*.
- WÜBBENHORST, H., effect of cold-rolling and annealing on Watt losses of dynamo and transformer steels, 120*A*.
- WULFF, J., iron powders, 95*A*.
- WYMAN, W. F., leaching of manganese carbonate ores, 41*A*.
- WYZALEK, J. F., Nicarb process of case-hardening, 63*A*.
- YARNE, J. L., defects in enamel coatings, 116*A*.
- YAROTSKY, M. F., co-operation between open-hearth and rolling-mill departments, 206*A*.
- YEADON, R., hydraulic plant in steelworks, 57*A*.
- YOCH, A. H., oxy-acetylene cutting machine, 21*A*.
- YORK, F. H., elected Member, 4*P*.
- YOUNG, C. B. F., electrolytic polishing, 186*A*.
- ZADRA, J. B.:  
 concentration of manganese-bearing ore, 131*A*.  
 concentration of manganiferous iron ore, 88*A*.
- ZAPFFE, C. A., defects in enamel coatings, 115*A*., 116*A*.
- ZENER, C., lattice expansion due to cold work, 25*A*.
- ZERFOSS, S., refractory materials, 162*A*.
- ZIMMERLEY, S. R.:  
 beneficiation of manganese ore, 194*A*.  
 concentration of manganese ore, 41*A*.

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